CHEMISTRY SIMPLIFIED.

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A COURSE OF LECTURES ON THE NON-METALS,
BASED UPON THE NATURAL EVOLUTION
OF CHEMISTRY.

DESIGNED PRIMARILY FOR ENGINEERS.

BY

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ILLUSTRATED BY ONE HUNDRED AND THREE ORIGINAL DRAWINGS.

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GENERAL

PREFACE.

In these lectures to mature beginners in Chemistry, the fundamental idea has been followed to unroll before the student the knowable nature of bodies as an ever-growing and spreading picture, and not as a finished work handed down by the great masters. When I say mature beginners, I mean that in my estimation chemistry should not be taught at all to boys and girls before their full mental growth has been attained, fully aware of my isolated ·position in the present evolution of schools. Only the mature mind follows with growing interest the unfolding of such a picture, and absorbs it as a living thing.

In following this fundamental idea, the usual systematic classification had to be abandoned. It will be seen that the beginning is made with bodies of familiar acquaintance such as the common metals, but these metals are not postulated as elements or simple bodies; they are merely objects for experimentation in allowing the equally familiar bodies of air and water to act upon them under the familiar impulse of heat. Noting the changes thus wrought, the mind questions and seeks answers. Answers come by carefully laid experiments, but always in

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such a way that no agent of unfamiliar nature is called in to aid.   Such a scheme is essentially historical, for the successive generations of chemists have been working in exactly this way.   They saw and raised questions.   Their answers, being premature in so far as they brought into play unknown agents, were often wrong, had to be set aside and much modified by subsequent investigations.   Thus also in these lectures, questions are raised, but not answered at once, although perfectly well known, because the student's knowledge has not reached the required fullness.   In the chapters on green vitriol and on common salt, as well as on potash, the reader will find the application of the fundamental idea fully elaborated.

Generalizations from the experiments are always drawn, though I have avoided the term law.   Theorizing upon molecules and the structure of molecules, ions and electrons I have omitted altogether. No beginning student can be capable of drawing inferences for himself concerning these matters. They should only be brought before the student at the end of his school work, if he intends following chemistry.   To bring them before proposing engineers, seems unnecessary, if not unwise, and these lectures are delivered to engineering candidates, more especially mining engineers and metallurgists. To them the theories can be of no help.   They want to know the practical consequences which must follow from the presence of certain material conditions.   They must be trained to inquire, and de-

duce from given conditions. The chief tendency
of the lecture course is to evoke in the student the
constant thought of Why? together with the love
for the experiment. The course extends over seven
months and one-half, in three lectures a week. It
is supplemented by laboratory work of eight hours
per week in which some fifty-odd experiments, se-
lected from the lecture experiments, are performed
by the student. The chemistry of the metals in
conjunction with qualitative analysis comprises the
second year's work of equal time-extension, but only
two lectures a week.

The illustrations are made with the chief aim of
engineering simplicity. Thanks are duly given to
each and every chemist who has given a laborious
life in contributions with which to build up the
chemistry of to-day.

THE AUTHOR.

HOUGHTON, MICHIGAN, *November 15, 1905.*

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CHEMISTRY SIMPLIFIED.

CHAPTER I.

THE NATURE OF AIR AS A MIXTURE OF GASES.

INTRODUCTORY REMARKS. I show you this small copper ingot. It was made by pouring liquid copper, at a yellow heat, into an iron mould. You notice a bright red color on the sides and bottom, a dark reddish-gray on the upper side, and a pale yellowish-pink on this spot which I scrape with the knife. By drilling a hole through the ingot, or by sawing it into two we find the pale, soft yellowish-pink color persistent throughout the interior. Hence we infer that the yellowish-pink is the *true color of copper,* while the red and gray-red at the outside must be due to a change which happened to the ingot during the time when it passed from yellow heat to the temperature of the room. If we do not take this change as a simple matter of fact, but if instead we ask for the reason of the change, then our mind is *scientific,* it is above the average, and there is hope for us. Now there are two ways for satisfying this desire for the reason for things. Along one way we just ask the nearest man or the handiest book, along the other way we set to work it out ourselves. Following the second and much harder road, we become investigators and inventors.

You have come here to learn chemistry, and my duty is to show you the way. I may lead you along the first trail by means of a book and recitations and my own acquired knowledge of the nature of things. However, I choose to take you by the second trail, difficult in steep slopes and rapid descents, but which will ultimately take you, when the pass shall have been won, into the beautiful valley of intellectual satisfaction and fruitful technical invention. Some may get exhausted on the journey, and some may not have the right eyes to see, the right hands to grapple with the difficulties; for them of course there is no hope and they must take the other trail, they will not become leaders in the profession. Those who are born with right desire will ultimately get to the goal by any road whatsoever; but they will have spent much time, much energy, in doing useless things. *My object, as your teacher, is to point out things to you so that you may save the waste and arrive much more rapidly at the pass.*

Let us return to our ingot and ask: What causes the copper to be of different colors on the outside from the inside? This question we name, by general consent, a *chemical question* because the change which happened to the outside of the ingot is a *permanent change*, by which the substance has acquired different properties throughout. If I bend this wire there is also a permanent change, but it is only a change of shape, the copper itself has not changed any of its properties. If we inquire about this change of form in the new positions of the copper

particles, we have to deal with a proposition in *physics*. There are, of course, many changes in which physics and chemistry overlap, when we must enter into both sciences. It is merely a matter of convenience, for the sake of more effective work that this division into physics and chemistry has been made. One set of men pursue the one set of phenomena, becoming more expert in observation than if they spread themselves over both sets.

1. *The nature of air.*

Pursuing the question concerning the changes at the surface of the copper ingot, we shall now institute experiments, every one of which will give rise to new questions.

In Figs. 1, 2, 3, 4 the trial arrangements are set up to meet those questions.

In Fig. 1, a bright piece of sheet copper *A* is placed within the non-luminous or purplish part of the flame *F*. It is evident that here the metal will be exposed to the action of heat, to the action of air and to the action of the substance of the flame. The metal at bright red heat, under these conditions covers itself with a dark scale, which peels off and is found to be very brittle. In Fig. 2, the metal *A* is within the hard-glass tube *T*, which is closed at one end, open at the other end. The substance of the flame does not come in contact with the metal, but the heat of the flame is conducted through the glass, the metal becomes red hot and covers itself with a very thin film. Here the air has access, but

limited. Fig. 3, shows the metal strip A within a tube T. The tube was then drawn out at C, leaving a narrow neck, was then connected with an air pump until all air was drawn out, when the neck C was allowed to close up by means of a sharp, hot flame (blow-pipe flame). If then the tube T be

FIG. 1.

FIG. 2.
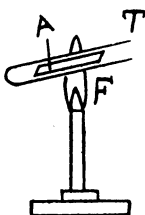
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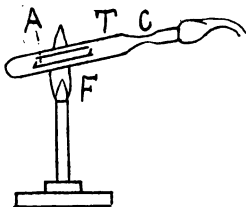
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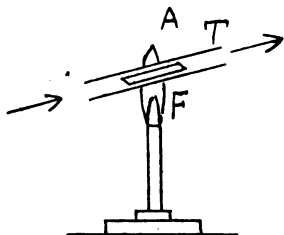
made red hot in the flame F and kept so for any length of time, we find, on cooling, that no change has taken place, the copper is bright with its fine pale yellowish-pink color. Lastly in Fig. 4, we have the copper strip in a glass tube which is open at both ends. Owing to inclined position a lively air current will set in in the direction of the arrows as

soon as the tube is heated by the flame.   We find
quickly that the last conditions produce the most
change on the copper—the most rapid development
of the scale.

Deduction from the four experiments: 1. Copper
takes from the air, at red heat, a portion of the air
and changes to a brittle scale.   2. The substance of
the flame does not enter into this change, only the
heat of the flame.   Two questions now suggest
themselves: 1. How much will be absorbed by a
given weight of copper? 2. How much of a given

FIG. 5.
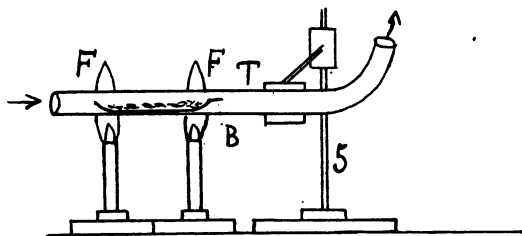
volume of air will be absorbed?   In order to an-
swer the first question rig an apparatus as shown
in Fig. 5, where T is an infusible glass tube (so-
called combustion tube) not less than $\frac{1}{2}''$ inside
diameter.   The tube is bent over the blast lamp.
Place the tube in a horizontal position by means of
clamp-stand 5.   Select a porcelain boat sufficiently
narrow to pass into the tube easily.   Clean and
weigh the boat.   We choose glazed porcelain
because it will not become soft except at white heat,
because it does not change in weight when heated

in air.   Place into this boat about 0.100 gram of
copper filings, that is to say you must take the
weight very accurately.   But it does not matter
whether you take 0.095 or· 0.102, only by taking
0.100 accurately you will save figuring the percent-
age.   You are told to take filings, because in this
form the metal will be exposed with a maximum
of surface and a minimum volume, which is most
desirable, since the intended action proceeds from
the surface.   Shove the boat into the tube as shown
in the figure, and place the lamp so that the entire
length of the boat can be brought to redness.   The
bent part of the tube being bent upwards, a so-called
draught will arise as by a chimney, because a col-
umn of hot air being in the vertical tube, this hot
air being lighter than the cold outer air, the latter
will pass in at the lower end and push out the warm
air, hence a steady air current will pass through the
tube in the direction of the arrow's pointing.   Allow
this action to proceed for 30 minutes.   Do not for-
get to place a few fibres of infusible asbestus between
the tube and the boat, for ·the tube may become
soft and cause the boat to stick.   Should the tube
exhibit a tendency to· sag you will prop it up at the
end by means of a piece of brick.   Remove the
flame at the expiration of the half hour, let the tube
cool down until it can be held in the hand.·   Pull
out the boat and weigh.   Return the boat to the
tube, replace the lamps and work for another half
hour.   Then weigh again.   If the second weight is
not equal to the first, you cannot be certain that the

copper has saturated itself, and a third period of
heating becomes necessary, and perhaps a fourth
until you get constant weight.   Many trials, made
with greatest care, show that 0.100 copper will in-

FIG. 6.
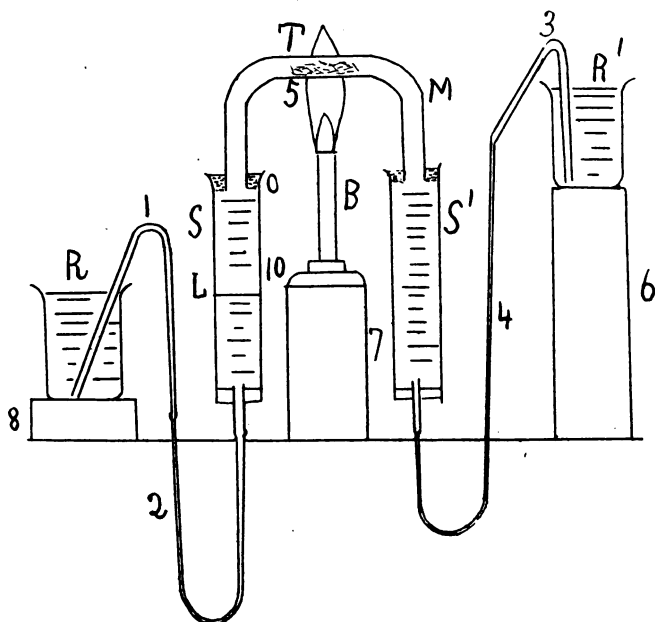
crease to 0.1254 and no further, and thus the result-
ing dark gray-black product of change will contain
in 100 : Copper 79.6 and air 20.4.

2. *How much will be absorbed from a given volume
of air ?*

For an answer to this question let an apparatus

be rigged as in Fig. 6. We must make provision
to pass and repass the same volume of air over the
heated copper without any air coming from the
outside, nor any air escaping to the outside. Let
T again be of hard glass $\frac{1}{8}$ or $\frac{3}{16}$ inch internal diam-
eter and 5 inches long. Introduce a roll of fine
copper gauze, 5, then bend the tube into a double L.
Paste on a mark at M. Determine or gauge the
volume of the tube by filling it with mercury up to
the mark M, and then weigh the mercury. If the
weight of the mercury be g, then $g/13.6 = V$ (in cubic
centimeters). Provide two soft glass tubes, S, S',
with stoppers, the upper ones to receive the tube T,
the lower ones to receive narrow glass tubes, which
are connected by rubber tubing, 2, 4, with the glass
syphons 1, 3. These stand in beaker glasses, R, R'.
Calibrate the tube S into cubic centimeters, the
lower side of the upper stopper forming the 0 mark.

Calibration. Stand S upside down, after a solid
stopper 1, Fig. 7, has been pushed into the 0 mark.
Then weigh out (to 0.1 gram) $5 \times 13.6 = 68.0$ grams
of mercury and pour this into the tube. Make a
scratch (with a glazier's diamond, with a sharp
splinter of quartz, or with a hard file) tangent to
the meniscus. Measure the distance from 0 to 5
with a scale or pair of dividers. Lay this distance
down a strip of white paper and divide into 5 equal
parts. Lay on these divisions beyond five for the
whole length of the tube. Then paste the strip
upon the tube so that the 0 marks fall together,
and then cover the paper on the outside with molten

paraffin. Thus your tube is calibrated into cubic
centimeters. Weighing out a defined quantity of
mercury is not quite so easy as it sounds. Proceed
as follows : Place a very small beaker glass upon
a so-called pulp balance (it were foolish to use a
fine balance because we only want to weigh as close
as 0.1 gram). Why? Because 0.1 gram of mer-

cury corresponds to less than 0.01 cubic cent., and
we do not care to read a volume closer than 0.1
cubic cent. It would in fact be quite sufficient
accuracy if we got any weight of mercury within
1.0 gram. Make a pipette with capillary outlet by
drawing out an 8″ x ⅛″ soft glass tube over the
lamp flame as shown in Fig. 8, and cut off with file
at point a. Fill this tube—by sucking—with mer-
cury, and let this latter flow into the beaker, until
the balance tips. The beaker has been previously
balanced by shot, and the required weight, 68 grs.,
has been placed upon the weights' pan. The first
finger closes the upper end of the tube at the
moment of tipping. After the apparatus (Fig. 6)
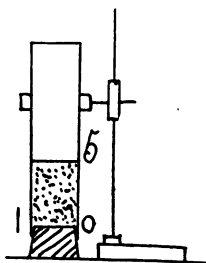
has been set up—the tubes S, S' being held in place by clamp-stands or tripods or under proppings—the beaker glasses R, R' are filled with water, the syphons 1, 3 are filled by sucking at the end of the detached rubber tubing until the water comes to the mouth, the rubber being then joined to the tubes S, S'. R' is then raised upon
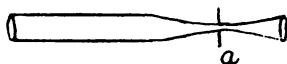
blocks until the water reaches the mark M, while R is lowered until its water level falls together with a division of the scale on S, say for instance 10.   We are having then a volume of air V equal to 10 plus v (v being volume of tube T). Let v be 5 c.c. for example; then the total volume will be 10 plus 5 equal 15 c.c.   Bring now the burner B under T so that the copper gauze 5 becomes red hot.   Cause the air to move slowly over the hot copper, by lowering beaker R' and raising R at the same time.   Repeat this movement 10 times.   Then remove the burner and let the tube T return to the temperature of the room.   Bring the water to the mark M and adjust R in such a way that its water-line and the water-line in S fall into one level.   On reading off the position of the water-line S on the scale, we will read 7, that is, 3 c.c. of air have disappeared; 15 c.c. of air have lost 3 c.c., 5 c.c. have lost 1 c.c.   Bring the flame

back and again pass 10 times over the hot copper.
On cooling will find the same result as before;
hence the loss of the air, under these conditions, is
constant.

Deduction.   Air is composed of at least two parts,
which possess each decidedly different properties, or
in other words : Air consists of two different gases.
Now it is well known that men and animals must
have air to breathe.   Query?   Which one of the
two gases do they require, or do they need both?
As the one gas has disappeared into the copper, we
shall have to experiment with the $\frac{4}{5}$ residuum.   Let
a glass jar *J*, Fig. 9, be filled with the gas.   How?   A
two-foot length of $\frac{3}{4}''$ gas pipe *2* (Fig. 10), is charged

FIG. 9.   FIG. 10.
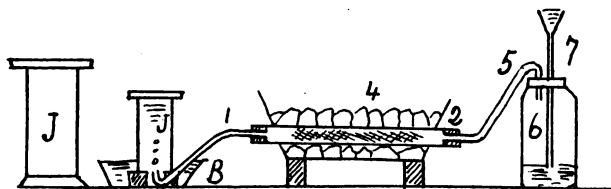
with copper gauze, and placed in a charcoal fur-
nace *4*.   Rubber tube *5* leads to bottle *6* through a
two-hole stopper ; so that the funnel stem *7* may pass
through second hole.   If water be poured into the
funnel the air will be driven through the heated
copper, and the $\frac{4}{5}$ residuum will pass through *1*
into the inverted and water-filled jar *J* whose open
end is supported under water by metal blocks in
the basin *B*.   We will now do a little figuring.   We

found above that 1 gram of copper can absorb 0.25 gram of air.   One litre equals 1000 c.c. of air and weighs 1.2932 gram, hence $\frac{1}{5}$ of this weight is 0.258, that is one single gram of copper is sufficient to take the absorbable gas from one litre or one quart of air.   50 grams of copper will furnish $(50 \times 4)/5$ equal 40 litres of the gas we desire.   But for our experiment, that is to fill the jar, we will not need more than one or at the most two litres supposing that the whole of the water has been displaced in J so that the bubbles will come on the outside.   We remove first the tube 1, then the supporting blocks and push a flat glass plate under the water, and press it with the hand against the jar rim, lift the jar out and stand it bottom down on the table as in Fig. 9.   A mouse having been trapped, we drop the animal from the trap into the jar and replace the glass cover plate.   At once the mouse shows distress, tumbles into a heap, and after a few spasmodic kicks lies quiet and is dead.   Hence we draw the conclusion that the part of the air which is absorbed by the copper, is the part also which sustains animal life.   If we introduce a burning taper into the jar it will become at once extinguished, and hence it follows with some considerable probability that breathing, burning and scale forming of copper are *similar* processes, being in fact, fundamentally, the same phenomenon.

It will be necessary, for clearness and conciseness of expression, to distinguish from now on these two parts of the air by separate names.   Properly we

should say—in English—life-air and death-air; instead Greek words are chosen by scientists. Life air equals ozone ; death air equals azote. The root of both words is Zoë equals life (zoölogy equals the science of living things). Ozone equals intense life ; azote equals no life. German chemists made and use the term, stickstoff equal to suffocating stuff; the French hold on to azote, English and Americans now use the word *nitrogen* which equals niter-producer.

Weight of one c.c. of nitrogen equals 0.001256 gram (Regnault).

Weight of one c.c. of air equals 0.001293 gram.

Hence it follows that ozone must be heavier than air. The weight of ozone follows by calculation.

We reduce azote to terms of air by dividing the weight of air into that of azote, 0.001256 / 0.001293 equals 0.97137 which equals the *specific* weight of azote or its specific gravity, then we have

$$\frac{4 \times 0.9713}{5} + \frac{x}{5} = 1; \quad x = (1 - 0.777)5 = 1.1145,$$

the specific gravity of ozone, and $1.1145 \times 1.293 = 1.441$, the weight of 1000 c.c. of ozone, and 0.00144, the weight of one c.c. of ozone.

Among the substances more or less familiar to every one of us is sulfur, which I show you now as crystal and massive as a broken lump. Light yellow color and translucency distinguish it from other bodies. If washed in water first, it yields no taste, it is insoluble in water. Against heat it is quite

susceptible. I place some of it upon this porcelain crucible lid and put the flame underneath. We see it melt quickly into a dark red-brown liquid, and then vaporize. Shortly after a blue flame appears and a strong, pungent odor permeates the air. The sulfur disappears slowly. Queries. 1. Is this phenomenon similar to that of the scale forming of copper, to the burning of the taper, to the breathing? Has either the ozone or the azote part in the disappearance? Let the flask _1_ be filled with air and a few c.c. of water as shown in Fig. 11. Take

FIG. 11.
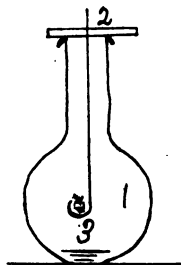
a strong iron wire _2_, hammer it flat at one end and rivet it to a small iron dish _3_. Put sulfur into the dish, beat the latter over a flame until the blue flame is strong, then lower the dish into the flask until the plate covers the mouth of the flask. The sulfur keeps on burning. Soon a white cloud obscures the flame. After some minutes we remove the spoon and notice that it begins to burn when it reaches the outer air. (Why? Because it again finds the ozone, which had become used up in the

flask.) We now shake the water and the gases together in the flask and pour out the water. It is somewhat turbid or milky ; after filtering it is clear, it has a sour taste and changes the purplish color of litmus to bright *onion red*. Litmus is obtained by extracting a lichen named by botanists *Roccella tinctoria*. The collected lichen is allowed to ferment in heaps, is then torn by a machine and allowed to stand with water, which assumes a deep purplish color; is used as a dye stuff under the name of *orseille*. Now vinegar has the same action, *i. e.*, a sour taste and turns litmus red. Vinegar (from French vin-aigre equal wine sour) arises when the sugary juice of grape or any other fruit, is allowed to stand in a warm place.

Wine results in a cool place. (Details will be given later.) The Latin name for vinegar is *acidum*, hence it came that later on all *sour* substances were and are called acids in English, French, Spanish, Italian ; but in German the word saüre = a sourness, and in Swedish syra, only differing in the vowel.

When Lavoisier, in 1781, had observed the above phenomena, he proposed the name *oxygène* in French, *oxygen* in English for what we have named ozone or life-air. The word oxygen is derived from the two Greek words oxus = sour, sharp, biting and genomein = to produce, to generate. This name we shall use in the future.

Definition : The combination of oxygen with a metal or non-metal is hereafter to be designated an

oxyd—oxid—oxide. The first spelling is the grammatically more correct, but the last spelling *oxide* is at present mostly used by English and American chemists. I myself use oxyd—the derivation is from oxydatus = oxydized.

Hence copper scale is now copper oxyd, the penetrating gas from burning sulfur is sulfur oxyd.

General deductions. Air being a compound of azote + oxygen and copper oxyd of copper + oxygen, they both seem to be representatives of the same type of bodies *i. e., compounds.* Whether all compounds are of one kind or not, we cannot, at this stage demonstrate. The term *compound* requires *single,* or *simple* as opposite. We will define as *simple bodies* or *elements* all those bodies which can be brought back from their compounds to their first condition *i. e.,* with all their previous physical properties. This definition is raised in our minds by the behavior of copper oxyd when heated in a closed tube with splinters of charcoal. At a red heat, the scale of copper oxyd becomes yellowish-pinkish. On cooling a spongy mass of the metal is seen, and the metal possesses all previous properties. Hence copper is a simple body or element. The question arises: Are all our well-known metals elements? Experiment on the same line as that with the copper, answers the query in the affirmative, though there will be found experimental difficulties with some. When zinc has been burnt in air, at high heat, into white zincoxyd, and when we heat this oxyd with charcoal, we will get no satis-

faction because the zinc only gives up its oxygen to the coal at a *white heat* which the glass tube cannot stand ; and moreover, at this high temperature zinc itself is a vapor. Special arrangements must be made in this case to catch the zinc vapors, which will first condense to a liquid and the latter will solidify into metal with all previous properties. Though we know as yet nothing of the nature of charcoal, we must surmise that it contains a body which has a stronger attraction or affinity for oxygen, at high heat, than the metal. Owing to this we designate charcoal as an *deoxydizing* substance, and the process itself we call *deoxydation.*

Copperoxyd + charcoal + red heat = deoxydation. That the charcoal forms a new oxyd during this action we surmise at once. Because we see no deposit of any kind on the charcoal or on the tube, we infer that this new oxyd is a gas at the ordinary temperature of the air. By using only the first letters as symbols, we can represent the processes thus :

Cu + O + red heat = CuO = oxydation.

CuO + C (charcoal) + red heat = Cu + CO = deoxydation.

Sulfur oxyd can be decomposed by passing it in a glass tube over heated charcoal. Sulfur will deposit in the tube ; hence sulfur is an element, according to our definition. Yet sulfur is not at all like the metals. As mentioned above, it is transparent and very brittle, melts at a very low heat and becomes a vapor at 250° C. Hence we at once make two classes of elements : *metallic elements :* copper, tin, lead, iron, and so forth ; *non-metallic elements :* sulfur, oxygen, azote, etc.

CHAPTER II.

THE NATURE OF WATER.

To us who are dwelling on the shores of a great lake, or to the inhabitants of the seashore, the idea must early present itself that water must be of much importance in the household of our planet, but even to him, the savage, or half savage, who uses water merely to quench his thirst, water must be an object of veneration; and the inquisitiveness of the human mind must bring forth even in him a desire to learn more about it. The ancient thinkers, without experiments, said water is one of the primary, elementary things, and together with air, fire and earth, constitutes the great Quartette out of which comes the harmony or disharmony of all things. Man's body is made of earth and water, his soul of air and fire, thus combining within himself the four primary things. The elementary nature of water was undoubted up to the end of the 18th century. The traveler becomes acquainted with good water and bad water; water which has a bitter taste, an astringent taste, a salty taste, a nauseous taste. He learns to distinguish between Spring water, River water, Swamp water, Sea water. It was early observed that water combines with fire, and thus produces the scalding steam which would lift the cover off a pot.

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Water becomes a solid, transparent block under the influence and sway of chilling Boreas, the Northwind. To this splendid and fleeting thing the Greeks gave the name *Krystallos*, sometimes *Kryos*, and thus became the founders of *Crystallography*, because when they found the beautiful transparent *Rockcrystal*, which we now call *Quartz*, they considered it as a sort of *permanent ice*, and also called it Krystallos. Thus the name was applied much later to all bodies which exhibit geometrical outlines. Remember this connection between ice and crystal. More wonderful seemed the snow, and it took much hard thinking and much controversy until snow was admitted to be merely frozen rain. You throw your snowballs and skate over the ice and never once think anything at all, except that it is a part of Winter's fun, and yet for a hundred years men have been studying the form of snow-flakes, and each one found something new.

Physical properties of water. Reference is here made only to so-called distilled water, that is, water which has been in the form of steam at least twice, and which has only been kept in *porcelain* crocks. All other water is impure in differing degrees.

Water is a liquid between the temperature of 0° and 100° C. Below 0° C. it is solid—ice—brittle, and yet to some extent plastic, that is, capable of deformation under strong, slow pressure. (Bending of glaciers when plowing over undulating rocks.) Ice is colorless in small pieces, in great masses it shows a green or sometimes a deep blue color.

Water is without taste (distilled water); hence not pleasant to the palate. It is without color when seen in a bottle, flask or jar; but when looking through a long column it becomes more and more blue, that is, all but the blue part of the sunlight becomes absorbed. The finest effect is seen off the Savoy shore on the Lake of Geneva (Switzerland), where the rocks fall abruptly into the water to a depth of 980 feet. The ocean looks blue-black, but this is not water which can be compared to distilled water, whereas the water of the Geneva Lake is remarkably pure, having a steady and strong outflow in the Rhone River.

A litre of water at $+ 4°$ C. weighs sensibly more than at $0°$ C., hence ice will float on water. If, however, the temperature of water is raised by heating it will loose in density and soon the block of ice will sink to the bottom.

Water *dissolves* all solids, some very slightly, others in large quantities. Note this very important property. The purer the water the more energetic is the solving action. It attacks and slowly dissolves ordinary glass, but porcelain very much less, and platinum and gold still less.

Water absorbs all gases, some to a large extent, others to a very small extent. Hence the purest distilled water will not remain so but for a very short time. For absorption begins as soon as the stopper is removed, in fact has already set in before, unless the vessel had been full up to the stopper. As a rule all absorbed gases can be expelled by prolonged boiling.

Chemistry. The first query will be: Is water a simple, elementary body or is it a compound? Having observed that air can be broken up by metals and by sulfur at a red heat, we shall be consistent if we subject water to the same treatment. We start, therefore, with the assumption that water *is not* a simple body. The experiment will presumably proceed under proper conditions if a hard glass tube *T*, Fig. 12, with perforated stoppers be placed horizontally with a boat holding finely granulated zinc or iron filings in the middle of the tube. A glass syphon *5* reaching into the beaker is con-

nected by rubber *1* with stopper *2* while a clamp *3* permits a stop to the flow of water as well as a regulation of the rate of inflow. A delivery tube *5* leads just under the surface of the water in basin *6* and a test-tube *7* filled with water stands ready to receive any gases which might result from the action.
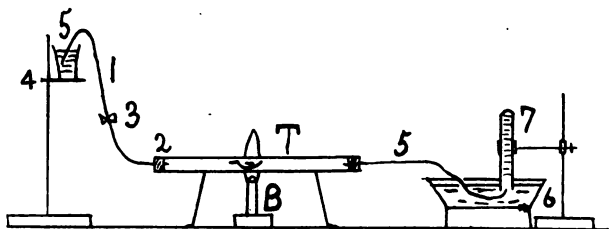
Let the flame from the burner *B* be now put under the boat and water admitted drop by drop at *2* so that a small pool forms behind the cork. As the heat extends along the glass tube the water will

begin to pass into steam and the steam will push out the air. When the latter is all out the steam will condense in tube *5* and of a sudden water will rush from *5* into *T*, will run to the red hot place at the boat and the *T* cracks. The apparatus is not up to the requirements. Why should not an iron gas pipe do in place of a glass tube? Since we are studying the action of steam upon the metals a metallic tube can do no harm, and any sudden inrush of water cannot injure the tube. Let therefore a gas-pipe of similar dimensions be substituted. A further advantage of such a tube will be that a higher degree of heat can be applied—say by means of a gas blow-pipe.

1. *Action on bright iron turnings.*

A gas is generated which we collect in the test-tube. It possesses an unpleasant odor and burns with a faintly colored flame. The chips have lost their brightness, they have become gray-black, and when struck with the hammer a brittle scale comes off. The scale is attracted by the magnet the same as the chips themselves. *Deduction:* This scale, resembling in every respect ordinary blacksmith's hammer scale, which is made by heating iron in air, like the other metal scales, leads us to conclude that water must contain oxygen.

2. *Action upon granulated zinc.*

Gas of the same character but odor less pronounced. The zinc is either converted wholly or

partly into white or grayish-white powder, or into a shining lustrous crust, which under the microscope shows six-sided prisms and pyramids. Character same as *zinc oxyd* obtained in air.

3. *Action upon copper turnings.*

Gas does not appear until tube has become yellow hot, and comes sparingly. Has no pronounced odor, but, burns. The copper has become bright red from the brittle *copper oxyd.*

The three trials demonstrate that water is a compound, not an element; and further, that it is an *oxyd*, in which oxygen is united with the other body, the latter appearing in the free state as a light, odoriferous gas.

Reverse proof. Collect the gas in a large bottle (use arrangement for collecting as in the case of azote). Stand the bottle *1* (Fig. 13) containing the gas upright. Its stopper holds the long funnel tube *2*, with rubber connection and clamp *3* and the delivery tube *4* which connects with the drying tube the latter being filled in the bulb with absorbent cotton and in the cylinder with burnt lime. Tube *6* is drawn out into a fine point (not too fine), and the glass cylinder, open at both ends, is held by a clamp and stand as shown in figure. If now water be run from the funnel into bottle, the water will drive the gas through, and if a burning taper be held to the tip of *6* two things can happen: either a steady flame *8* or an explosion which may shatter the tubes. (1 volume of the gas mixed with

2½ volumes of air explodes violently.) To avoid explosion, let the gas go through the tube for a while—until the water has risen in the bottle about one inch—and then only apply match or taper. The flame is first colorless, but soon burns of an orange-yellow color. Why? Because the glass, at a red heat, gives particles to the flame. Prove this

FIG. 13.
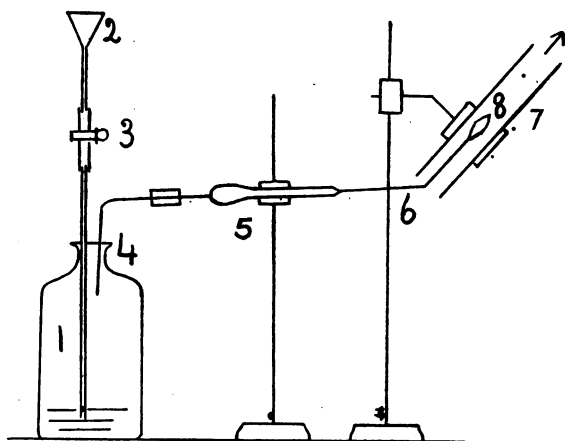
by placing a nozzle of silver, platinum or gold over the tube. The flame will then be invisible or nearly so, faintly purplish.

But the important part is that immediately when the flame appears the glass cylinder 7 becomes clouded and soon large drops of liquid condense upon the glass which will even collect and run from the lower edge of the tube. We find all the physi-

cal properties of distilled water in this liquid: Equal weight per equal volume; absence of taste and smell; equal resistance to passage of light; change into solid at 0° C.; change into vapor at 100° C.; very high resistance to the passage of the electric current; equal capillarity, by which is meant that both liquids rise in a very narrow or hair tube equally high above the outer level. Therefore, it is proper to apply the name *hydrogen* to this gas. *Hydor* = water, *genomein* = to produce: ·the body which produces water. It follows that water must be *hydrogen oxyd*.

ELECTROLYSIS.

Next to heat we find electricity as the most intense force, or probably both are only different manifestations of the same force, since heat can be made to generate electric current, and an electric current converts itself into heat under proper conditions. We will not investigate the generation of a current here and simply assume it as given; you will get the explanation in physics. We simply accept the fact that if I fasten this wire to the one binding post on the table and this other wire to the second post, and if the wire ends be brought in contact there is now flowing a current from one post to the other. If I break the contact a minute blue spark is the visible proof that a current was passing, but does not pass now. Why? The air space between the wires does not carry the current, air being a *non-conductor*.

In Fig. 14 a beaker glass is filled with distilled water; after bending the wires at right angles I sink the vertical portions into the water. The needle on this galvanometer does not move, hence it follows that the water between the two wires is as much a non-conductor as air; of course I speak relatively; it is a question of tension or pressure, for the current passes from cloud to earth in a

FIG. 14.
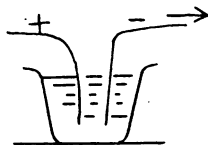
thunder-storm, and to say that air and pure water are bad conductors, will be a better expression than non-conductors.

If we substitute this Houghton spring water for the distilled water, we see the needle move, and hence deduce that the earthy materials which are dissolved in the water cause the better conductivity. An addition of salt to the water proves the correctness of the deduction. We see not only the diversion of the needle, but we see gas bubbles rise from the wires. The liquid conductor of the current is called *electrolyte.* The wires dipping into the latter are known as *electrodes.* The wire leading to the positive pole + is the *anode,* the one leading to the negative pole — is the *cathode.* They are always designated by the + and — signs.

If we arrange the apparatus as shown in Fig. 15, where *2* means a test-tube, filled with the electrolyte, and where the electrodes are spread, having strips of platinum sheet soldered to themselves, we will perceive at once—the current going through—that much more gas arises from the cathode than from the anode. On applying a match to the gas, after the test-tube has been lifted out, there is a strong

Fig. 15.
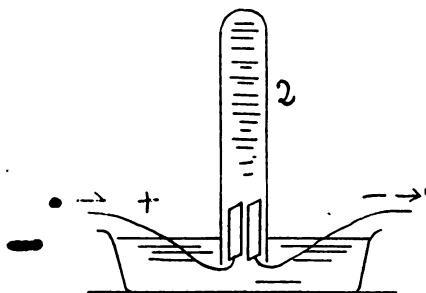
explosive sound; the tube may be splintered. We call the gas *fulminating* (lightning like). What is the nature of this gas? That two different gases are produced we find indicated in the larger volume of gas coming from one of the electrodes; and thus we are led to collect the two portions *separately.* Let us take two large test-tubes *B, B'* (Fig. 16) and blow into the closed end two narrow tubes *1, 2* before the blow-pipe. This requires some skill acquired by practice. To acquire such skill is very useful to any one who wishes to become a chemist; for glass-blowers are not always in the neighborhood.

However, in this case, we can avoid glass-blowing altogether by cutting off the closed end of the tubes by means of a file and a red-hot glass or iron rod. In

FIG. 16.
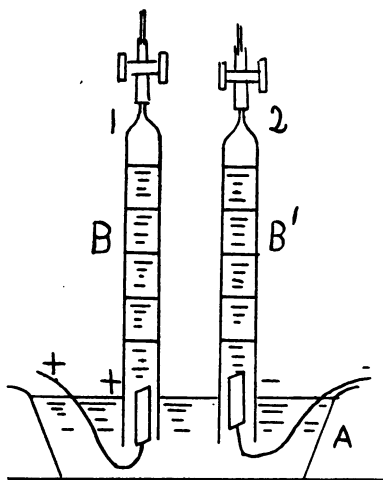
Fig. 17 you see the tube before and after cutting, and only a perforated stopper is needed with a narrow glass tube t, to which the short rubber tube with spring or screw clamp and a second bit of glass tube are attached. Calibrate now the tubes roughly into cubic centimeters. Fill the tubes with the electrolyte, hold them by a suitable stand in the basin A (Fig. 16), and insert from below the electrodes $+$ —. The current being turned on it soon becomes evident that the gas volume in B' is much larger than in B, that in fact the two volumes are as two

to one.   But in B' we have the negative pole, the
cathode ; in B, the positive pole, the anode.   When
B' is filled with gas to the electrode we stop the cur-
rent; draw out the electrode, shove a small cup
under the tube, lift the latter and bring it into a

FIG. 17.
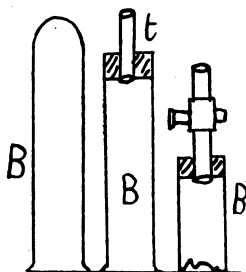
wide cylinder (a pail will answer, in default).   Now
if we press the tube B' down into the water until
there be a difference, H, Fig. 18, between the outer
and the inner levels, then the gas will be under a
pressure equal to the weight of a column of water
of the height H, and if the clamp C be cautiously
opened the gas must issue at P.   We notice first the
absence of any smell ; the absence of acidity, and
then apply a taper or match.   A flame appears at
the point.   A cold porcelain dish held in the flame
covers itself with moisture.   In fact the gas acts
exactly like the Hydrogen which we obtained pre-
viously, except that it has no odor.   The former gas
must have held some odoriferous body admixed.
(Supposition which must be verified at a future

stage.   As careful investigators we must heed every
difference of action.   In this instance we shall find
that zinc and iron contain small quantities of cer-

FIG. 18.
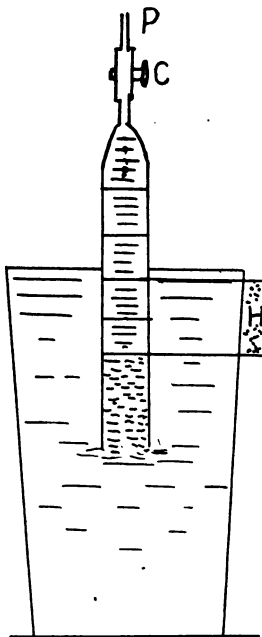
tain other elements, which combine with hydrogen,
producing strongly smelling gases.)

We proceed to operate now with tube *B* (Fig. 16)
by transference to the pail or large beaker.   The
gas has neither odor nor taste.   On bringing a match
over the jet no flame, but the coal of the match
burns with intense light. . A piece of red-hot copper

or iron wire held into the current, burns with strong light into a scale which has all the properties of copper oxyd, iron oxyd.

The gas shows therefore in an intensified form the behavior of air. It must be *oxygen*. That it is only oxygen we can prove by heating a given volume of iron or copper filings over mercury. On cooling the mercury will fill the entire tube ; all the gas has been absorbed.

Deductions. 1. Water is a chemical compound of the two simple bodies, hydrogen and oxygen. It must be a chemical compound because water is a body showing altogether different properties from those of a mere mixture of the gases as we have it in fulminating gas.

2. Elements combine according to simple ratio of volumes, as water is composed by volume of 2 hydrogen, 1 oxygen. If the letters H and O stand for the two elements then the symbol

$$H^2O = \text{water} = \text{dihydrogen monoxyd}$$
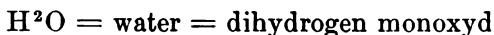
expresses this relation.

Inverse proof of this proposition.

Let E (Fig. 19) be a graduated or calibrated glass tube, near the closed end of which are fused into the glass 2 platinum wires $(+ \; -)$. Such a tube is known as *eudiometer* = splendid or perfect measure. Let it be furnished with a jacket J made of a wide glass tube (lamp chimney); a cork C holds it against the eudiometer. A narrow glass tube leads from the boiling flask F through the cork into the jacket ; th is a

thermometer.   Introduce about 10 c.c. of fulminat-
ing gas into the eudiometer, the mercury standing
as in the figure.   If now the water in *F* be kept
hard boiling until the thermometer shows 98° to
100° C., the volume of the gas will have increased
considerably.   Let us say it reads 11.0 c.c.   Connect
the platinum wires with poles of an induction coil,
also known as Rhumkorf coil from the inventor's

FIG. 19.
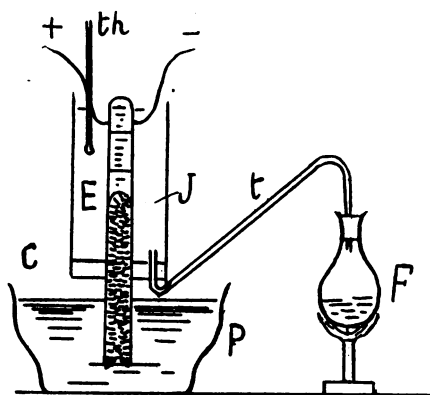
name; a spark will pass between the platinum wire
ends in the eudiometer with a considerable shock.
(Hold the eudiometer with the hand to prevent its
being lifted clear of the mercury in *P*.)   On read-
ing now the volume, we find it shrunk to 7.3 c.c.
A contraction has taken place of 3.7 c.c. or *one-third*
of the original volume.   Stop the steam, draw off
condensed water, and let come to the temperature of
the room.   The mercury will rise steadily until it

fills the entire tube, except a bubble of water at the very apex.

Explanation. The high temperature of the spark causes the union of the hydrogen with the oxygen, and at the temperature of 100° C. water is in the form of steam. The steam occupies two-thirds the space which was occupied by the mixture of gases. The union therefore caused the mass particles of the gases to approach each other at a fixed distance, so that three occupy now the space of two. 2 vols. H + 1 vol. O give 2 vols. steam. As the temperature sinks the steam becomes water and thus the mercury can fill the tube because the quantity of steam expressed by 7.3 c.c. corresponds only to a few milligrams of water, for 1 c.c. of steam at 100° C. weighs 0.0005896 gram, hence 7.3 c.c. = 0.0043 or 4.3 milligrams, which in the form of a drop of water is barely distinguishable with the naked eye. The 11 c.c. of gas must have possessed the same weight of 4.3 milligrams.

Law. Whenever gaseous elements unite in the ratio of 2 : 1 a contraction of one-third ensues.

Comparing the weights of the 3 gasiform elements which we have now discovered and studied to some extent, we find that hydrogen : oxygen : azote = 1 : 16 : 14. Oxygen is 16 times heavier in equal volume than hydrogen, and azote 14 times heavier. Therefore H²O represents 2 + 16 = 18 weight units and if the *smallest mass of each of these bodies, still capable of receiving a chemical impetus and acquiring thereby an active force or momentum,* be de-

3

signated as *atom*, then the figures 1, 16, 14 may be designated *atomic weights*, because the ratio will be the same as long as the volume is the same, for the largest as well as the smallest units.

Hydrogen peroxyd, H^2O^2.

Under certain conditions H and O can form a higher oxyd or *peroxyd* (*per* meaning beyond). This is a body of unstable nature; it falls to pieces easily but possesses extraordinary activity as an oxydizing agent. We shall study the mode of its preparation later as well as its application.

CHAPTER III.

GREEN VITRIOL OR COPPERAS.

UNDER the name *copperas,* which is the corrupted form of the French *couperose*, and the latter even a corruption of the Latin *cupriaerosa*, which means the "Rose of Cyprus," a substance of most marked properties has been known from time immemorial. We see it as bluish-green fragments and also in the form of large crystals. The symmetry of the faces can be reduced to the monoclinic system. Thin pieces are quite transparent and show very little color; because the depth of color is determined by the partial absorption of certain portions of sun light. The thicker pieces absorb more light in the transit of the latter and therefore have a deeper color. The substance is very brittle; it can be crunched between the fingers. Has a strongly astringent, bitter-sour taste, and is quite soluble in cold water, but very much more soluble in boiling water. The solution is not clear, but murky from a brownish-yellow, suspended substance. By filtering through paper the solution becomes clear. If such a clear solution be left standing exposed to the air, one notices the rapid forming of a yellow film on the exposed surface. The film becomes thicker and in time the liquid turns into a yellow brown,

mud-like fluid. Query? Has the oxygen of the air anything to do with this change, or the azote? This is easily settled by bringing some of the fresh, clear solution into a tube filled with azote and closing the tube tight. No change occurs. Another portion in a tube filled with oxygen, the film appears. Oxygen does the work. If the solution of copperas comes together with oak bark, the latter turns speedily black (in reality deeply blue-purple). It also turns leather black because the latter forms when raw hide is allowed to soak in water and ground oak or hemlock bark. We can extract the leather-forming substance from the bark by means of water and this solution turns black with copperas. Thus came into existence our black writing ink, already known to the ancient Egyptians. When the extract of bark is evaporated on a water-bath, a faint yellow-ish scale, very light and fluffy, remains: *tannin* (from tan). Copperas + water + tannin = ink; mucilage is added to give the ink a better body.

The Germans use the word *vitriol* instead of copperas. This name was first used by Pliny who lived 1900 years ago. He describes the substance as "*vitriolus quasi vitrum.*" Vitrum is Latin for glass, the crystals resembling green glass were yet easily soluble in water, while glass is not soluble. Glass is fairly hard, this substance not, hence vitriolus, a kind of glass, like glass in some ways. We shall use the word vitriol as being better expressive of the substance.

CHEMICAL INVESTIGATION OF GREEN VITRIOL.

Let a hard glass tube ($\frac{1}{8}$ to $\frac{1}{4}''$ internal diameter and 6 to 8 inches long) (Fig. 20) be closed at one end over the gas blow-pipe. Hold the tube in nearly horizontal position or rather lower at the open end, the

FIG. 20.
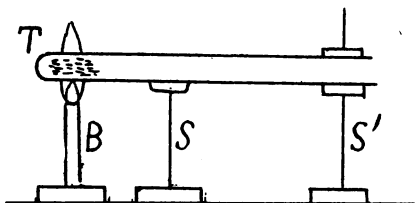
closed end being charged with several small pieces of vitriol. Let the tube be supported at S, because it has a tendency to sag when the end comes to a red heat. It stands to reason that the tube may be laid upon a couple of bricks for support. Let heat be applied slowly with the burner B to the closed end, and we will be enabled to make the following observations: 1. A plentiful condensation of a liquid in the cool part of the tube. This liquid will appear very mobile, little or no taste and by applying electrolysis will give $H + O$; its identity with water is fixed. 2. The vitriol meanwhile, is partly melting, raising blisters and turning into a white chalky mass.

Deduction 1: The loss of water causes the vitriol to become white opaque. We raise the temperature to a low redness: A strongly smelling gas appears re-

calling the smell of burning sulfur, that is the **oxyd**
of sulfur S^nO^m. We cause it to act on indigo and **lit-
mus** solutions, the former becomes bleached, the **lat-
ter** turns red; probability strong that vitriol contains
sulfur oxyd though not certain yet. But remem-
bering that copper oxyd is decomposed by **charcoal**
at red heat, we may attempt the decomposition of
this suppositious oxyd in the same way—and with-
out much of an outlay in apparatus. Let some
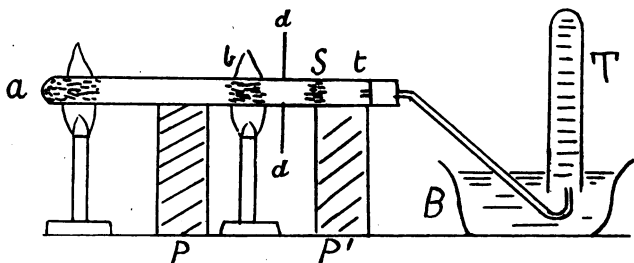
vitriol be heated in a porcelain crucible until it
has become white, that is, until the greater part of
the water has been removed, then fill it into a tube
exactly the same as before, that is, at the closed end
a, Fig. 21.   Let some splinters of charcoal be heated
in a *covered* crucible at full red heat, and when cooled
down introduce them into the tube at *b*; stopper the
tube with cork and gas evolving tube *t*, the latter
leading into basin *B* filled with water.   The water
filled test-tube *T* is held ready to be shoved over
the end of *t*, when it may be assumed that the air
has been quite driven from the apparatus by the

evolved gases. The closed end a is first brought to redness, then the charcoal at b is brought to dull redness, or any other degree of temperature we may find advisable. If the gas be decomposable exactly as copper oxyd is decomposed, we must get

$$S^n O^m + 9\,C = S^n + m\,CO + (9 - m)\,C,$$
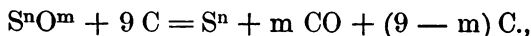
but since sulfur is a *non-metal*, it is quite probable that compounds of S and C are generated, for which we must look out. The glass tube is best supported by two bricks, P, P', stood up on edge. In order to facilitate the deposition of sulfur we protect the part of the tube beyond the charcoal with a diaphragm or screen d. The latter can be a slotted piece of sheet-iron or a piece of asbestus board. As soon as the charcoal becomes red at one spot, we notice a film forming before the diaphragm, which increases in bulk, forming yellow and yellow-brown drops. The water in the basin becomes turbid, milky, and a gas of peculiar smell collects in the test-tube. What causes the milkiness? What is the peculiar smell due to? These questions we shall not attempt to answer at this juncture, but place them on the calendar for future study and explanation. We let the tube cool down, cut it with file and hot glass rod at the diaphragm, and subject the yellow film to two tests. (a) We scratch out a portion of the unknown yellow substance, place it upon a piece of bright silver foil, and heat it over a flame, until the foil is barely red hot. When cold a black spot or possibly a hole will appear, where the unknown

substance was placed, the silver has formed a black compound and this is *characteristic for sulfur.* (b) We hold the tube inclined to get draught and heat the film in the flame; we get the pungent odor of burning sulfur. No doubt can remain, vitriol contains sulphur oxyd, or at any rate we can say that this gas is one of the products when vitriol is broken up by heat.

Now let us return to the original experiment which we left in order to prove the sulfur oxyd. We apply now a very hot flame (best from a Bunsen gas blow-pipe) to the vitriol. White clouds appear in the tube and roll out of the latter; the substance of this fume is evidently heavier than air. The action of it upon the mucous membrane is energetic, for a suffocating sensation is caused by inhaling it. It causes the muscles of the larynx to contract vehemently. At the same time, with the appearance of the fumes, we notice a thick liquid condensing at a little distance from the heated end of the tube. We let the latter cool down and cut it off just at the liquid ring; as the two pieces come apart another installment of white fume appears. Why? We apply litmus-paper to the liquid; it turns intensely red, but soon after turns brown, and finally the rim gets black; the paper has been charred. Deduction: The liquid possesses qualities of an extraordinary nature. The great experimenter who discovered it in the 10th century, the Moor Geber in Spain, gave it an Arabic name which was translated into Latin: oleum vitrioli—*the oil of vitriol,*

owing to its sluggishness in flowing like a thick olive oil, and because it produced a lubricating of the skin when rubbed between the fingers. In order to study the substance, we must design an apparatus which will allow the treatment of a considerable quantity of the vitriol, say one pound. Since we noticed that the glass became quite soft and even collapsed when exposed to the high temperature of the blow-pipe, we must look out for a material which will remain solid as well as rigid at such a temperature. Fire-clay is such a material. Its

FIG. 22.
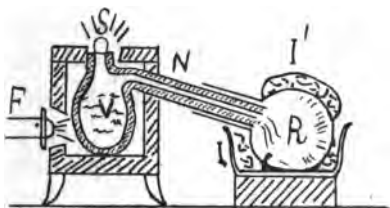
plasticity when mixed with water makes it capable of being moulded into any desired form. When carefully dried and then equally carefully baked, it becomes hard, fire-resisting, and fairly gas-tight.

In Fig. 22 we see the section of a fire clay *retort* inside of a fire-brick lined furnace, which is heated by a gasoline flame *F.* Before filling the vitriol into the retort, we heat it in an open dish or large crucible until all the water is driven out, and until it has turned a light brick red, that is, at a low red heat, since we only care for the white, cloudy fumes

and not for the sulfur oxyd. Then we fill the ma-
terial V through the tubulature at S and fasten the
stopper or plug by means of pasty fire-clay. Over
the neck of the retort N, we pass the neck of the
large glass flask R loosely, to furnish exit for the
gases. The flask we bed into a mixture of salt and
broken ice (freezing mixture) contained in a basin I
and over the upper side of the flask we spread a
muslin bag I' filled with the same mixture. Why?
In order to expose a maximum of cold surface to the
fumes, having seen in the preliminary experiment
that the fumes do not condense at the ordinary tem-
perature. The lid of the furnace having been put
in place, we light the flame under strong air pressure
and soon the retort will show cherry redness on the
outside. But since the fire-clay wall of the retort is
but a poor transmitter of heat, some further time
must elapse until the material V gets to that temper-
ature. Then we see the white fumes pouring into the
flask, falling like a foaming cataract to the bottom
and also issuing at the neck of the flask. Hence the
apparatus should stand under a good up draft or
alongside a good down draft. The heat will be mod-
erated or increased according to the volume of white
vapor issuing from the neck N. If no more fume
comes—say after two hours—even at a yellow heat
of the retort, we stop the operation. We remove the
basin I and the bag I' and wipe the outside of the
flask dry. Three facts are observable: A brownish
thick liquid about 50 c.c.; snow-like crystals of needle
shape all over the flask; and a dense fume still filling

the flask.   We pour the liquid into a large test-tube, or into a smaller flask.   During this operation quantities of the white fumes arise suffocatingly from the liquid, wherever the air touches it.   Query?   Which constituent of the air causes this action?   Azote, oxygen or the water vapor?   By experimental elimination we fix the action upon the water vapor = moisture, of the air.   *Without moisture no fumes.* Hence it follows that the roasted vitriol must still contain *some* water, or else we could not see the fumes inside the glass tube in our first experiment.

Two immediate investigations must now be undertaken; we must first try to get at the inwardness of the crystallized substance, and secondly, of the liquid substance.

a. Investigation of the *oil of vitriol,* the liquid substance.   If put upon the skin, a drop will raise **a** blister and actually burn a hole into the flesh, destroying the tissue thoroughly.

Brought together with a drop of water a hissing sound is caused.   If water be splashed or poured into a larger quantity of the oil, so much steam is generated by the evolution of heat, that the liquid is thrown violently from the vessel and has often injured the careless operator.   Paper is charred into a slimy, black substance by the oil.   White sugar and starch are changed into the same black substance.

The oil smells strongly of the sulfur oxyd gas, and when heated emits white fumes, until at the end a liquid results, nearly colorless, which does

not fume at the air, and does not smell of sulfur oxyd. This colorless liquid boils at 326° C. (a very high temperature), giving likewise dense white fumes to the air, when boiling, which condense into a *colorless heavy liquid*, thus differing from the white fumes of the oil, which condense into a *snowy solid*. With an arrangement as in Fig. 23, we can prove

FIG. 23.
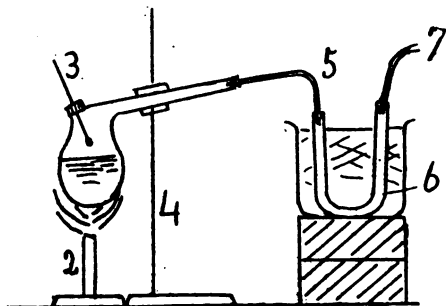
these points. In the small retort on the left of the figure we place some 10 c.c. of the oil of vitriol, using a long-stemmed funnel, so that the neck shall not be moistened with the liquid.

At *3* we have a thermometer not reaching into the liquid ; fasten it into the tubulature with asbestos thread. The retort is held by a clamp from stand *4*. At *5* we have a U-tube connected by a narrow tube with the neck of the retort through a cork. The U-tube is also fitted with perforated stoppers and stands between broken ice—or snow—in the beaker glass *6*. Any liquid, condensing in the retort's neck,

will flow back. Heating with burner *2* using a very small flame, we soon get the smell of sulfur oxyd alone at *7*, and later on associated with white fumes. At the same time the walls of the U-tube become frosted over with white, needle-shaped crystals. When the temperature has risen to 300° C., we stop heating and remove the U-tube ; noticing the fumes arising from the cold substance in the tube, as soon as moist air comes in contact with it. Now let us change the position of the retort by turning the swivel of the

FIG. 24.
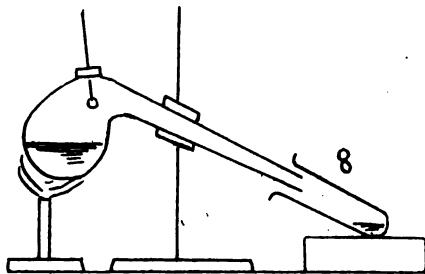
clamp holder. The neck points downward, Fig. 24, and reaches into a dry test-tube. Raise the heat so that the liquid gets into boiling commotion. Streaks and streamers of thick liquid will run down the neck and collect in the test-tube *8*. Hence it follows that by heat we can split the oil of vitriol into three parts : a gas (sulfur-oxyd); a solid (?); a liquid residue (?). The question-marks stand for : *must be found out.*

The liquid residue. Let it be acted upon by the metals. Bring about 2 c.c. of the liquid in a test-tube

together with a piece of copper foil.   No action is
noticeable until we heat, when effervescence ensues.
(Effervescence means frothing due to rapid produc-
tion of gas bubbles in a liquid.)   The smell charac-
terizes the escaping gas as sulfur oxyd.   Further we
notice the forming of a grayish, granular substance,
and the copper foil has disappeared ; it has become
changed or converted into the white granular sub-
stance.   These interesting facts lead us to a suppo-
sition or hypothesis that our liquid must contain an
oxyd of sulfur containing *more oxygen* than the gasi-
form oxyd.   If the latter be symbolized as S^nO^m,
then the hypothetical oxyd would be S^nO^{m+p} in
which symbol p denotes the mass units of oxygen
which were given over to the copper enabling the
latter to go into solution, through the abstrac-
tion of this oxygen from the higher oxyd to form
the lower sulfur oxyd with its characteristic smell.
But in order to verify the supposition we must ex-
amine the white granular product of the action.   We
pour off the liquid, add water to the granular resi-
due, and see it go rapidly into solution with a pale-
blue color.   The solution we evaporate on a water-
bath.   At a certain point of the evaporation a solid
begins to form.   We allow the liquid to cool and a
larger crop of blue crystals will form.   The crystals
are translucent, show an oblique symmetry, in fact
resemble the crystals of our original vitriol.   Hence
the deduction will be rational that the crystals are
copper vitriol.   (A crystal placed upon a knife blade
with a drop of water produces a bright copper spot

upon the blade.) We dry the crystals between filter paper and bring some into a closed tube. On heating, as in the original experiment, we observe water first, and the vitriol turns white. At higher heat, full redness, we note some sulfur oxyd gas, and at still higher heat, when the glass begins to melt, a ring of oily liquid (oil of vitriol). On cooling the vitriol has become *jet black*, and the black body, under the circumstances is evidently *copper oxyd*. The chain of evidence is complete. This copper oxyd must have been contained in the copper vitriol. And having put metallic copper into the liquid, the copper oxyd can only have formed by taking oxygen from a higher oxyd present. The latter is an oxyd of sulfur, because sulfur oxyd forms during the operation. We symbolize the operation or action thus:

$$pCu + 2pS^nO^{m+p} = pCuO.S^nO^{m+p} + pS^nO^m.$$

A vitriol thus defines itself as the combination of a metallic oxyd with *sulfur peroxyd*, the syllable *per* meaning more. Both vitriols contain water, but that does not mean that *all* vitriols must contain water.

ACTION OF THE LIQUID RESIDUE UPON LEAD AND SILVER.

If we bring a piece of lead foil or very thin sheet lead into a test-tube with the liquid residue, there is no action at the ordinary temperature. On heating we notice a whitish film on the metal which again disappears. But on further heating there is at once

an impetuous action, with formation of sulfur oxyd gas and a very fine granular white substance. Likewise a yellow streak appears in the upper part of the tube. Lead vitriol is white and remains white when we add water, and furthermore does not dissolve even in a very large amount of water. We collect the white substance on a filter, wash it thoroughly and let it become dry in the air. In the closed tube, when heated to redness it gives *no water*, but over the gas blow-pipe it decomposes leaving yellow lead oxyd, the latter entering into combination with the glass at this high heat, forming a yellow transparent compound.

The yellow streak on the upper tube we can readily prove to be sulfur. We crack off the tube near the streak, wash thoroughly with water, dry and then heat over a flame. The yellow streak will melt and then burn with a blue flame, giving the smell of sulfur oxyd. This fact teaches us that, while under ordinary conditions a metal takes from sulfur peroxyd only enough oxygen to convert the peroxyd into the oxyd, under extraordinary conditions of stimulated chemical activity, the oxygen may be taken away altogether from the peroxyd, leaving sulfur in the free state.

We bring a piece of silver foil into the liquid residue and heat, when action sets in, the foil disappearing, without being changed into a solid residue; in other words, the silver vitriol is *soluble* in the liquid. If water be added to the cooled liquid, cautiously, a white crystalline powder will

soon fall out, but will again dissolve when much water is added, that is, the silver vitriol is soluble in water and soluble in the concentrated liquid residue, but not soluble in the moderately dilute liquid residue.   Of the solution of the silver vitriol we will soon be able to make some important use. Gold is *not* attacked by the liquid residue, and hence a very important deduction follows that if gold and silver are united in the form of an alloy, they may be separated by means of this liquid residue, and are thus separated in the Mint and the Metal Refineries.

INVESTIGATION OF THE SOLIDIFIED OR CRYSTALLIZED WHITE FUMES.

We take now the U-tube which contains the snowy deposit.   We notice the inner surface of the corks strongly blackened (same action as shown by the oil as well as the fumes, even at ordinary temperature). On pulling the cork white fumes develop (again like the oil).   We let a drop of water run down the side of the glass.   A hissing noise is produced, and a drop of heavy, oily liquid, runs to the bend of the U.   By adding drop after drop of water, we convert all the solid, snowy substance into the brownish-colored liquid, which latter, by this time, has become burning hot.   We act with this liquid upon the metals as we did with the Liquid Residue.   The action is exactly the same in both cases, forming vitriol and sulfur oxyd.   Hence it follows that the solid product from the distillation of the oil of vitriol, or in other words, the *white fume* must be *sulfur peroxyd*.   But

4

then it follows inversely that if the sulfur peroxyd
be converted by water into a liquid, whose action is
the same as the Liquid Residue, then the latter
must be sulfur peroxyd plus water. Stated sym-
bolically this means—

White fume $= S^nO^{m+p} =$ Sulfur peroxyd.

Liquid Residue $= S^nO^{m+p}. H^2O =$ Sulfur per-
oxy-hydroxyd.

Sulfur oxyd $= S^nO^m$.

Oil of Vitriol $= S^nO^{m+p}.H^2O + S^nO^{m+p} + S^nO^m$.

And since sulfur oxyd and sulfur peroxyd are
expelled from the oil by heat, we express the pre-
vious condition by saying: Sulfur oxyd and sulfur
peroxyd are *dissolved* in the *sulfur peroxy-hydroxyd*,
and thus form the oil of vitriol. The latter is a
stable compound of the two oxyds, which cannot be
broken up by boiling; it distills over at 326° C.
without decomposition. Instead of saying sulfur
peroxy-hydroxyd we will say in future *sulfuric acid*,
because the substance has eminently the characters
of an acid body; but the other name expresses
better its make-up.

DIRECT PROOF OF THE PRESENCE OF WATER IN THE SULFURIC ACID.

By holding before us the actions of this sub-
stance upon the metals which we have observed we
can deduce, among others, the following reasoning:
(a) If lead is converted by the acid into a vitriol,
i. e., a combination of lead oxyd with sulfur per-
oxyd plus sulfur oxyd we must get lead vitriol also,

by bringing together lead oxyd plus sulfuric acid
without the forming of sulfur oxyd.   (b) Lead vit-
riol does not take up water.   (c) Therefore if we
mixed thoroughly an excess of yellow lead oxyd
with a certain quantity of sulfuric acid, then the
water must be liberated if any be contained in the
acid.

In order to reduce the argument to trial, we shall
mix 5 c.c. of concentrated sulfuric acid with 50
grams of yellow lead oxyd in a small wedge-wood
mortar until the paste is almost powder.   We fill
this into a test-tube.   Place the latter in a horizon-
tal position as shown in Fig. 25, where T is the tube

FIG. 25.
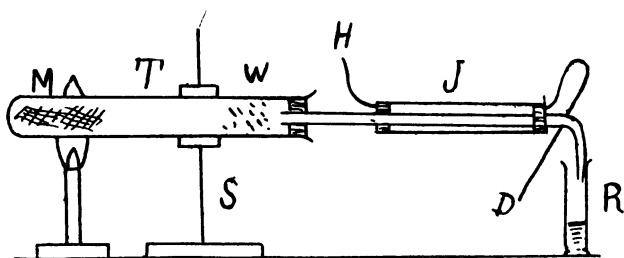
holding the mixture M with a delivery tube passing
through the jacket J fed with cold hydrant water H,
which runs through the discharge tube D into the
sink.   Almost at once, after applying a flame gently
back and forth under M, a condensation of mobile
liquid, water in fact, takes place at W, much steam
passes into the tube, is condensed by the cold jacket
and collects in test-tube R.   The first distillate is

nearly, not altogether, pure water. It will show acid reaction to litmus; but if one cubic centimeter be drawn out and weighed, the weight will be so nearly one gram, that for our purposes we may accept it as one gram and thus experimentally show the sameness with water. We have proved that sulfuric acid is

$$H^2O.S^nO^{m+p,}$$
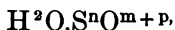
or in other words that it is a vitriol in which hydrogen oxyd takes the place of other metallic oxyds.

SO^2. We have arrived at a stage of development when we will be able to reason out the ratio in which sulfur and oxygen are united in the gasiform sulfur oxyd. Let us make a bent (knee-shaped) tube K, Fig. 26. Fill it with mercury and hold it with a

FIG. 26.
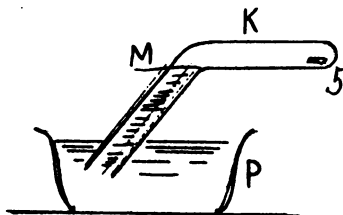
proper clamp and stand in the mercury trough P. By heating a certain peroxyd (known as potassium chlorate) in a test-tube we can easily make pure oxygen gas and cause it to rise in the knee-tube until the mercury shall drop to an arbitrary mark M. We will then shove a piece of sulfur under the opening and let it rise to the surface. A piece of soft copper wire rolled into a spiral at one end will

enable us to push the sulfur to the end of the tube
at 5. A strip of gummed paper can now be used to
mark the new mercury level. If a flame be now
brought under *5*, by slow degrees to avoid crack-
ing the glass, then 5 be strongly heated to the
point of ignition of sulfur, we will suddenly see
the mercury get into strong up-and-down motion.
This means that union between sulfur and oxygen
has taken place. Heating is stopped when the mer-
cury has become quiet. When the apparatus has
returned to the temperature of the room, we find
that the mercury has risen to the mark. Hence it
is evident that oxygen changes into sulfur oxyd
without change of volume. Or we can say one volume of S^nO^m contains one volume of O. But how
much sulfur has entered into the volume? Evi-
dently we find this by subtracting the weight of one
volume of oxygen from the weight of one volume of
S^nO^m. Let the latter be W′ and the former W,
then

   W′ — W = S′ (weight of sulfur in the gas).

Now we need only to know how much one vol-
ume of sulfur weighs to solve our problem. These
values have been determined and reduced to air as
unity ; they are

1 vol. S^nO^m = 2.210 : hence W′—W = (2.21 — 1.105)

1 vol. O = 1.105 :   = *1.105*

1 vol. S = 2.200 :   = S′

                 : so S′ = $\frac{1}{2}$ S

                 : because $\dfrac{2.20}{2}$ = *1.10*

hence follows SO^2 as expressing the volume ratio between the two bodies.

Thus we see that $1\frac{1}{2}$ volumes of the free gases when combined only occupy one volume—condensation of one-third. The same was true of hydrogen and oxygen when they combined to water.

If the true numerical symbol for sulfur oxyd be SO^2, which we necessarily pronounce *sulfur dioxyd,* what is the symbol of the *sulfur peroxyd?* The answer is SO^3. You will prove this yourselves at a later stage of this course, and just simply accept the fact. The vitriols are therefore:

$H^2O.SO^3 =$ Hydroxyd vitriol $=$ Sulfuric acid.

$CuO.SO^3 =$ Copper oxyd vitriol $=$ Copper vitriol.

$PbO.SO^3 =$ Lead oxyd vitriol $=$ Lead vitriol.

$ZnO.SO^3 =$ Zinc oxyd vitriol $=$ Zinc vitriol.

$FeO.SO^3 =$ Iron oxyd vitriol $=$ Iron vitriol $=$ copperas.

$Ag^2O.SO^3 =$ Silver oxyd vitriol $=$ Silver vitriol.

The writing of silver oxyd Ag^2O is based upon experiments and reasonings which we cannot now go into, but which will appear shortly.

The dilution of sulfuric acid. If we make that experiment in which we proved the presence of water in the liquid residue or the *concentrated* sulfuric acid, with great care, weighing the acid taken and weighing the water which results, we obtain in a given experiment, when we took 20.54 grams of the acid, 3.77 grams of water; hence the concentrated acid contains in 20.54 grams: SO^3 equal 16.77; $H^2O = 3.77$. We also know that $S = 2O$,

that is, the sulfur as gas weighs for equal volumes twice the oxygen, S = 32, therefore

1 sulfur $= 32 \times 1 = 32$.   Also $2H = 2 \times 1 = 2$
3 oxygen $= 16 \times 3 = 48$.   1 oxygen $= 16 \times 1 = 16$

<div style="text-align:center">——</div>

<div style="text-align:center">Sum 80   Sum 18</div>

The numbers 80 and 18 stand for the mass units of SO^3 and H^2O, or as other chemists say, they represent their *molecular weights*. The experiment gave us

$$SO^3 = 16.77 : 80 = 0.2096 : 1$$
$$H\ O = 3.77 : 18 = 0.2094 : 1$$

By dividing into these numbers the molecular weights, we change the weight numbers into molecular quantities. We get *equal* quotients and have thus established that the symbol $H^2O.SO^3$ is the true quantitative expression for that concentrated acid, which distills without breaking up.

We take this concentrated acid and add water, mixing the two; the mixture becomes hot. We conclude of necessity thàt a chemical union has been effected. Let the addition of water be rational instead of arbitrary. Let the quantity of concentrated acid taken be 100 grams, which contain : SO^3 $= 81.6$; $H^2O = 18.4$. By adding with a graduated tube or cylinder 18.4 c.c., we will have added just one other mass-unit of water; the resultant liquid will be

$H^2O.SO^3.H^2O = $ *sulfuric acid monohydrate,*

containing in 100 parts: $SO^3 = 68.9$; $H^2O = 31.1$. After this liquid has resumed the normal tempera-

ture of the room, we take of it again 100 grams, add to this 18.4 grams of water, and mixing, find again a rise of temperature, but much less than before. Unquestionably another chemical union of lesser strength of hold, the

$$H^2O.SO^3.2H^2O = \textit{sulfuric acid dihydrate,}$$

containing in 100 parts: $SO^3 = 58.2$;. $H^2O = 41.8$. Repeating the operation a third time a very slight rise in temperature follows.   Hence we conclude that the

$$H^2O.SO^3.3H^2O = \textit{sulfuric acid trihydrate,}$$

containing in 100 parts: $SO^3 = 49.2$; $H^2O = 50.8$ is the last hydrate.   Beyond this figure water is not held in chemical, only in mechanical, union, which we can very properly express by the symbol

$$H^2O.SO^3.3H^2O + aq.,$$
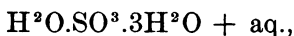
in which aq. stands for Latin aqua = water ; this is *dilute* acid.

ACTION OF HYDRATES OF SULFURIC ACID UPON THE METALS.

The mono- and di-hydrate act in a boiling solution the same as the acid upon lead and copper, that is, SO^2 is disengaged and the vitriols form.   The trihydrate does not act upon lead or copper. . But if we bring this trihydrate upon zinc or iron a violent evolution of gas results.   The gas, however, is not SO^2. It has a peculiar odor, more marked with the iron than with the zinc.   But the gas is inflammable, and if the flame is inside a cold test-tube, water

condenses fast.   The gas is, therefore, mostly hydro-
gen ; the odor coming from other bodies contained
in the iron and zinc, so-called *impurities*.   The pro-
cess may be represented by symbols, thus

$$H^2O.SO^3.3H^2O + aq. + Zn = ZnO.SO^3 + 3H^2O$$
$$+ aq. + H^2,$$
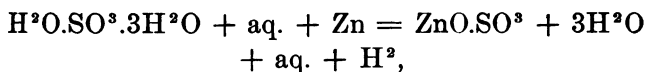
for if the liquid be evaporated after the action, zinc
vitriol crystallizes.   In other words, we may de-
scribe the process thus : Zinc oxyd has a stronger
tendency to form vitriol than hydrogen oxyd.   The
zinc therefore takes the oxygen away from the latter
and thus liberates hydrogen.   We may extend this
idea to the former reaction, where SO^2 is evolved,
thus

$$Zn + H^2O.SO^3 = ZnO.SO^3 + H^2.$$
$$H^2 + H^2O.SO^3 = SO^2 + 2H^2O.$$
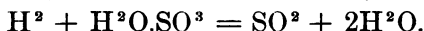
The power inherent in " nascent " hydrogen is such
that it will decompose SO^3 into $SO^2 + H^2O$, but
this power does not exist in the dilute solution.   The
result is just the same as if we say the metal, zinc
for instance, takes the oxygen from SO^3.

Acting upon iron chips with dilute sulfuric acid,
we get finally a muddy, dark-colored solution and
the hydrogen gas is strongly tainted with other gas
of a fetid, unpleasant odor.   When the liquid
stands, it gradually becomes clear with a bluish-
green color, a black sediment having fallen to the
bottom.   We remove this by filtration and find that
the dried, black substance can be burnt like coal ; it
is a peculiar kind of coal called graphite, and the

fetid gas is a combination of the coal with hydrogen
(C^nH^m). Zinc likewise leaves a residue, but this
does not burn. We shall see at a later stage that the
residue is due to certain metals and non-metals,
always present in the crude, commercial zinc. But
let us return to the bluish-green liquid. We will
evaporate the liquid upon a water-bath until a crust
forms over the surface, which signifies the beginning
of crystallization. Then we set it away over night
and find next morning a crop of greenish crystals.
They are identical in form with the vitriol we
started our experiments with; they also act in the
closed tube in the same way, when heated. We
have thus a direct proof that vitriol, the so-called
copperas, is iron vitriol. Yet when we take the
red solid residue obtained from the destructive heat-
ing of the copperas, and boil that body with sulfuric
acid and trihydrate, we get a *yellow* solution, from
which, by evaporation, yellow, scaly crystals are
deposited. This is an undoubted vitriol, but not
copperas, yet containing all the elements of the
latter. Hence no other deduction is possible than
the following: There must be *two oxyds of iron*, as
we found a red and a black oxyd of copper, an SO^2
and an SO^3. These oxyds are presumably FeO
and FeO^2. But which of these is in copperas, and
which is in the yellow crystals? A very neat little
process of inductive reasoning will give us the an-
swer. It has been observed at the beginning of this
chapter that when a solution of copperas in water
stands exposed to the air, a yellow film will form at

the surface.   That this must be due to the action of
oxygen, because in azote, no such film comes into
being.   We can accelerate the forming of the yellow
precipitate by blowing air into the liquid.   If we
dissolve this yellow solid (after separating it from
the liquid by filtration) in dilute sulfuric acid, we
get, after evaporation, the same yellow crystals as
we did from the red oxyd + sulfuric acid, and if we
heat the yellow substance (not the crystals) we get
in fact the red oxyd.   Therefore it follows that cop-
peras contains the lower oxyd, and the red oxyd is
the higher oxyd.   Just how the proportions of oxy-
gen and iron stand we cannot, now, prove; but let
us assume that this proportion is 1/1 for the lower
and 2/3 for the higher oxyd.   Then we can write

$$Fe + H^2O.SO^3 + aq. = FeO.SO^3 + aq. + H^2,$$
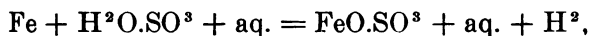
but we can explain, even now, why we get so much
SO^2 in the earlier stages of vitriol distillation.
Namely : SO^3 we saw is a strong oxidizing agent,
and hence the lower iron oxyd changes at its ex-
pense into the higher oxyd.

$$2(FeO.SO^3) + 7H^2O + heat = 7H^2O + SO^2 + $$
$$SO^3 + Fe^2O^3.$$
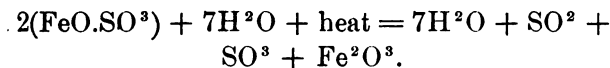
We must of necessity get just as many molecules of
SO^2 as we can get of the more useful oil forming SO^3.

  Practical application of some parts of the lesson of
oil of vitriol.   1. How to prepare, on occasion of
need, sulfur dioxyd (SO^2).   A 250 c.c. flask *2* is
filled to about one-half with thin lathe chips of cop-
per.   The stopper funnel *1*, Fig. 27, is filled with

sulfuric acid monohydrate. *B* is a burner; *4* a wash-tube partly filled with water; *5* a drying tube, one-fourth filled with concentrated sulfuric acid, and *6* a bulb tube filled with glass beads which have been moistened with concentrated sulfuric acid. Why? Because up to a certain point we have

FIG. 27.
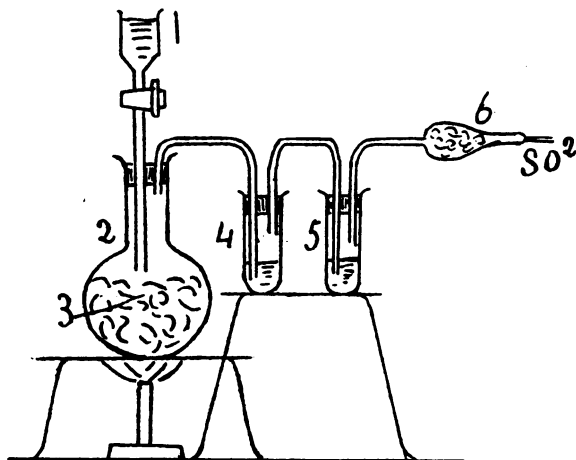
found an extraordinary attraction of this acid for moisture. Now if the acid flows from *1* into *2* upon the chips, while heat is properly applied, a stream of pure SO² will soon displace all the air from flask and tubes, so that presently pure, dry gas issues from *6* ready for any desired purpose. When *dry* gas is not required, the tubes *5* and *6* are left out. After the chips are used up, the flask must be cleaned out; it is best though to clean it out immediately after the

need is past, because the vitriol will become as hard
as rock and the flask be much in danger.

2. *How to Generate Hydrogen.* This substance is
very often required, and in large quantities, for
filling a balloon, for instance. For small quantities
you may use the apparatus just preceding, Fig. 27.
The flask *2* is partly filled in this case with granu-
lated zinc, and dilute acid is fed into the funnel *1*.
Make the acid 1:20, that is, 20 volumes of water
for one volume of the acid. You will find that
such a simple contrivance is all right for a small
volume of gas, but not for more, and what you do
get comes very fast at first, then ever slower. Why?
Because the dilute acid becomes a solution of zinc
vitriol, which renders the acid more and more weak.
Many devices have been designed to get a better
result. The adjoining figure, Fig. 28, shows my
own design, which has given complete satisfaction
to all those who gave it an intelligent trial. The
principal part of the apparatus is a glass tube *G*
drawn slightly into a neck *N*, and at the lower end
into a narrow tube *O*, to which latter is fitted a
stout rubber tube *R*. The latter forms a U, has a
glass nozzle *P*, and thus discharges the dilute solu-
tion of zinc vitriol into the glass jar *W*. This tube
G, which we better name the "generator" is filled
with the granulated zinc. It is surrounded by a
wider tube *J* which is melted at both ends together
with the generator, thus forming a jacket. The
latter can be filled with water through the tubula-
ture *E*. The function of the jacket is to keep up a

Fig. 28.
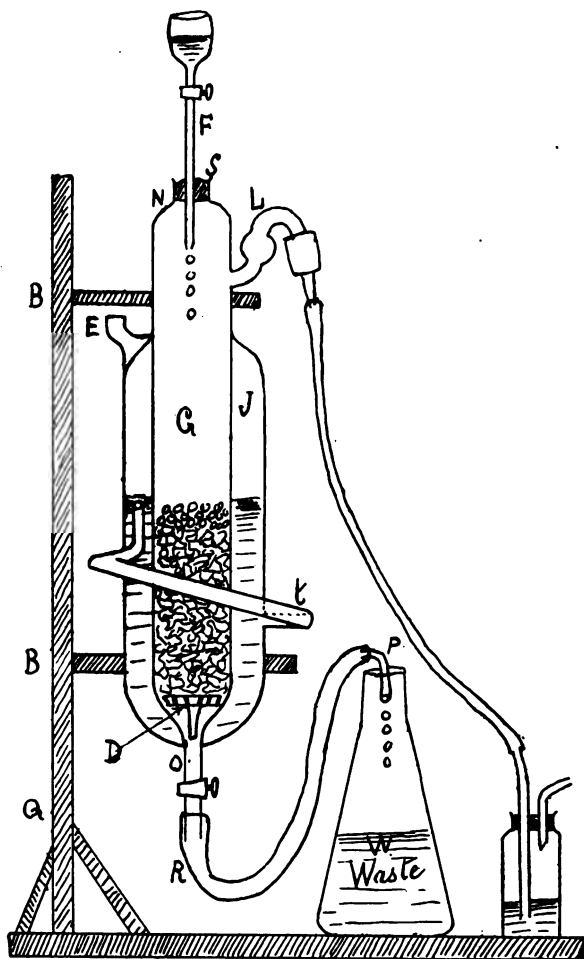
KOENIG'S GENERATOR.

temperature of about 70° C. in the generator. To this end a 5-millimeter glass tube *t* has been melted into the jacket obliquely. The middle portion of the tube is of brass and is here heated by a little flame which burns from a glass tube or from a Bunsen burner. A rubber stopper closes the neck *N* and through it passes the funnel tube *F* which should be 12 inches long. The whole apparatus is held in vertical position upon two brackets which may either be attached to a portable stand *Q* or may be put against the wall under the hood permanently. The zinc is prevented from falling into the rubber tube by the "false bottom" *D* made of porcelain. After the jacket has become hot you fill the bulb of the funnel with the dilute sulphuric acid 1:20, and also fill water into the generator until it begins to run from the nozzle *P*. Now open the stopcock of the funnel so much that a drop falls from the stem every second, and soon a steady stream of hydrogen will issue from the tubulature *L*. The gas will be free from air sooner than in any other form of generator. The gas will be washed and dried as shown above. When the column of zinc has fallen by three inches, it should be filled up ; but that includes a steady running for a whole day. For much use, a large reservoir bottle, holding the dilute acid, should be rigged up above the funnel, so that the acid can be drawn into the cup of the funnel by means of a syphon.

CHAPTER IV.

THE LESSON OF LIMESTONE.

WE have before us three productions of nature, which to the eye are very different. The first is a large crystal of *dog-toothed spar, calcspar* or *calcite,* quite common in our copper mines, notably at the Quincy Mine, where it is intimately associated with the native copper. This particular crystal comes from the zinc-lead mines of Joplin, S. W. Missouri. You will notice that one end of the crystal shows three lustrous faces intersecting over the edges at an angle of a hundred and five degrees nearly—a rhombohedron—whilst the other end shows six faces intersecting at alternately different angles — a scalenohedron because the faces are scalene triangles—thus producing the impression of a dog's fang. Parallel to the faces of the rhombohedron the mineral cleaves perfectly. I cleave off a piece and you see a small rhombohedron exactly *similar* to the original one. It is both colorless and transparent, and if placed upon this cross upon white paper we see the lines of the cross *double;* the two images are close together. The physicists say the mineral has double refraction and give you an explanation according to the present state of their knowledge. From this property the mineral is

(64)

sometimes called double-spar (the latter word, *spar*, is given to all minerals which are more or less transparent and show strong cleavage).

The second specimen is this whitish rock which is known as *crystalline limestone*. It shows numbers of small but splendent faces, each of which is in reality the face of a rhombohedron similar to that of the calcite : or in other words the rock is made up of innumerable calcite rhombohedrons which prevented each other from developing individual geometric independence.

The third specimen is this dull gray rock commonly known as *limestone*. In its appearance there is nothing in common with the previous specimens. But all three possess nearly the same relative weight (specific gravity), and an equal power of resistance to a penetrating steel point (equal hardness). The comparison thus far made we call *physical*, meaning therewith that all the given properties have been ascertained without destroying the identity of the original substance. Let us now act upon these materials with the powerful agents in our possession, whereby the original identity will become modified or wholly destroyed, new bodies being produced. The knowledge thus gained will be *chemical* knowledge, and will greatly widen out our horizon as to the nature of things.

1. *Action of heat.* Place a fragment of calcite in a glass tube closed at one end, and heat this end to high redness. No odor ; fragment turns dull chalky. It might nevertheless be that an odorless

5

gas is evolved.   Contrive a rig as sketched in Fig.
29, wherein t is the hard glass tube with the frag-
ments. $B B$ are two bricks to concentrate and re-
flect the heat rays upon the tube. T is a test-tube
filled with water and t' a short bent glass tube at-
tached to t by a short piece of rubber tubing.   The
heat may be produced by means of a blast lamp or
by placing over the tube t several pieces of charcoal
made incandescent and by then fanning them into
combustion by an air blast or by means of an ordi-

FIG. 29.
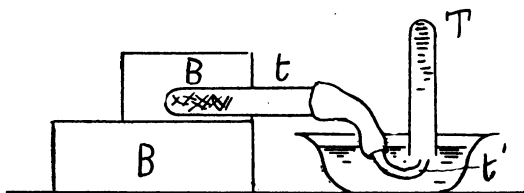
nary fan.   The heating with coal is much more
satisfactory than with the blast lamp.

When the tube has come to red heat, we observe
a steady current of gas bubble through the water
into the test-tube.   The gas is odorless and evi-
dently not soluble in water to any considerable ex-
tent.   Now we found the gas from the copperas to
give a sour taste to the water, aside from the strong,
pungent odor; hence we examine the present gas in
the same direction.   Water is not changed to the
taste but blue litmus paper is slightly reddened.
We say the *lime gas* has a weak acid nature.   It
does not burn or explode as hydrogen and does

not stimulate or increase a burning as oxygen.
It is of all gases thus far encountered most like
azote. But in making soap bubbles with it, the
latter immediately fall to the floor; hence the gas
must be much heavier than air or azote (the latter
being $\frac{4}{5}$ of the air) and moreover azote does not im-
part sour or acid properties to the water. Thus we
are forced to the conclusion that this lime gas is a
new body. But if so, we ask, is it a simple or com-
pound body? In order to find answer to this ques-
tion, let us do some reasoning by comparison: The
copperas or iron vitriol is crystallized or transpar-
ent; it has been proven to be composed of two
oxides + water. Calcite is crystallized and trans-
parent, gives off a slightly acid gas and leaves a
white opaque solid. Hence we will be justified in
the assumption that calcite also is composed of two
oxyds, one metallic, the other non-metallic.

$$X^n O^m . Y^p O^q$$
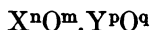
This is an *hypothesis* (the word is the Greek equiva-
lent for either supposition or assumption).

Proof for the gaseous or volatile part. If the gas be
an oxyd like water (as steam) it may be possible to
break it up by a metal such as zinc, or, as we saw
with the oxyds of iron and copper, heat and char-
coal might do it. Let us choose zinc in the form of
these bright chips. It will be necessary to produce
a small but steady current of the lime gas. Having
seen that both dilute sulfuric acid and vinegar can
decompose the calcite and the limestone, we choose

the vinegar. Why? Because the latter gives a soluble product, whilst the sulfuric acid gives a milky solution or a white mush, an insoluble vitriol. In the flask F (Fig. 30) bring about 20 grams of finely ground calcite or limestone with about 50 c.c. of water. Into the funnel V pour concentrated vinegar acid, acetic acid, because the Latin word for vinegar is *acetum.* With the help of a small flame a steady current of gas can be made for quite

FIG. 30.
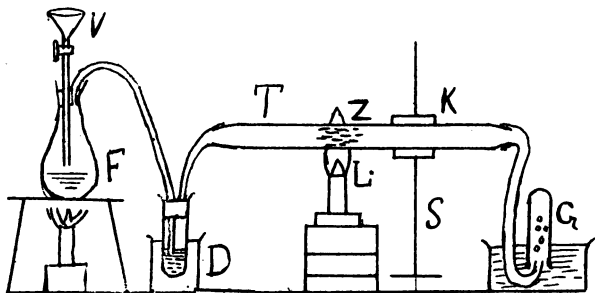
a while, admitting more acid in small portions as needed. In the hard-glass tube T at Z lay the zinc chips between two asbestus plugs. The flame L will bring Z to red heat. Stand S with clamp K holds T in position. But since we want to prove an oxyd, it is evident that such proof would become impossible if the gas were to enter T at once, for the gas is charged with water vapor and we know that water will yield oxyd when brought together with red-hot zinc. We therefore interpose the test-tube D which is partly filled with concentrated sulfuric

acid, through which the gas will have to rise in
bubbles. We do this because we found that oil of
vitriol absorbs water with very great energy. It is
a *dryer*. Had we not observed well and noted this
property we would now stand before an impassable
obstacle. But going as we do, the discoveries come
apace with their immediate practical application.
Now we begin the generation of the gas. The
latter, being heavier than air, forms a steadily
thickening layer over the liquid in F, driving the
air before it and out of the entire apparatus. We
keep on patiently until at least two volumes equal
to F have been generated to make quite sure that
the air is completely displaced. For if any remain
our results could not be conclusive, since some zinc
oxyd would surely be formed, whether the lime gas
were an oxyd or not. Zinc is coming to redness; a
white cloud appears on the glass. But in order to
find what becomes of the gas let a rubber tube be
brought under a test-tube G filled with water, and
it will be seen that the tube soon fills with a color-
less, inflammable gas. The zinc is oxydized. Now
we may assume that the inflammable gas is the
element Y or a lower oxyd of Y and symbolize thus:

$$Y^pO^q + qZn + \text{red heat} = Y^p + qZnO$$

or

$$Y^pO^q + Zn + \text{red heat} = Y^pO^{q-1} + ZnO.$$
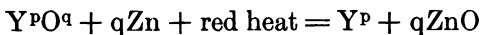
This alternative brings us up against the wall once
more. Unless we shall happen to discover a metal
with greater attraction for oxygen than the zinc, we
shall not be able to prove directly that the com-

bustible gas is an element or a lower oxyd. Let us
not despair; of wonders and signs of wonders there
is no end.

Study of the residuum. In order that this residue
may be as much freed from the gas as possible, let
us pour it from the glass tube into this platinum
crucible. This latter being infusible we may con-
centrate upon it a much higher heat than was pos-
sible in the glass tube. Lifting the lid we see the
pieces emit a white glow, whilst the metal of the
crucible is only yellow. We say the lime is highly
incandescent. The pieces still show the rhombo-
hedrons of cleavage; there is even luster upon the
faces. The volume is the same but the weight has
decreased 44 per centum. Cohesion has decreased.
This residue is known as *burnt lime—caustic lime*
(" caustic" being merely the Greek for burnt). It has
been known for ages to both civilized and savage
peoples. Since limestone forms the surface rock for
many square miles in large tracts of country all
over the earth, the first burnt lime was made when
the first man—living in a limestone country—made
a rough fireplace with the pieces of rock around
him. According to our hypothesis burnt lime
ought to be an oxyd X^nO^m, the oxyd of a metal X
whose properties we do not know. For if we try
upon this lime the same agents which yielded us
the metal from the oxyds of iron and of copper,
namely intense heat (by the blow-pipe) and char-
coal, our trial will end in failure; the white mate-
rial remains quite unchanged. What was said of

the final nature of the element Y above, applies here in regard to X. Let it stand for the present as X, or since we called Y the lime gas, let X be the *lime metal*. We may even designate by the symbol *Ca* (the first letters of the word calcite), since we designate iron by the symbol Fe (the first letters of the word *ferrum*); yet ever bear in mind that it is a suppositious, a hypothetical simple body of whose properties, in the first state, we are ignorant. This ignorance does not prevent us from studying the behavior, the properties of the supposed oxyd.

First towards water. Let a drop of water fall upon some of the caustic lime, a hissing noise ensues; a slight cloud of steam arises; the lime swells up and falls into an extremely fine powder: *Flour of lime.* The flour can be dried at steam heat and yet this dry flour will yield water in the closed tube, at red heat, and lose 24.3 of its weight. After cooling moisten the lime and it will hiss with water as before and fall into flour. Hence we say the burnt lime has a very strong affinity for water, and will form with it a true union, a chemical compound, a *hydroxyd*, very much as the sulfur oxyd SO which forms the hydroxyd we called sulfuric acid. Deduction: *Both metallic oxyds and non-metallic oxyds form hydroxyds.*

Flour of lime $=$ lime hydroxyd $= Ca^nO^m.H^2O$.

Adding more water the lime hydroxyd turns into a *white paste: Slaked lime.* If we add much water, shake and stir thoroughly and then let stand, we notice that apparently the whole of the white paste

will settle, leaving a clear liquid above. Deduction : Lime hydroxyd is very little—if any—soluble in water. However, the water has a decided taste, and turns reddened litmus paper to *blue*. Hence it is an agent, and we call it *lime water*. By evaporating 100 c.c. in a weighed dish, we obtain a residue of hydroxyd of 0.1 gram—1000 lime water hold 1 hydroxyd.

Second, towards acids. Make a $\frac{1}{10}$ p. c. solution of sulfuric acid and of vinegar or acetic acid. Because sulfuric acid has a specific gravity of 1.83, we will require 0.054 c.c. to give us 0.1 gram (1.83 : 1 = 0.1 : 0.054), that is, just one small drop for the 100 c.c. of water. The strongest acetic acid has sp. grav. 1.05, nearly the same as water. Two small drops of it will give the strength wanted with 100 c.c. of water. Pour 25 c.c. of each of these very diluted acids into 2 beaker glasses, add a little *litmus* solution to each, which will produce red color. Now slowly add clear lime water from a graduate into the first beaker glass. All at once the red color changes to blue, when a certain number of c.c. have been added. The same with the acetic acid. We deduce : The two bodies of opposite action to litmus saturate each other so that a *neutral* body results, the neutral body is the *salt*. Let M stand for any metal, and N for any non-metal, then

$M^n O^m . H^2 O$ = hydroxyd = *base*

$N^n O^m . H^2 O$ = hydroxyd = *acid*

$M^n O^m . H^2 O + N^n O^m . H^2 O = M^n O^m . N^n O^m$ (*salt*) +
$$2H^2 O$$
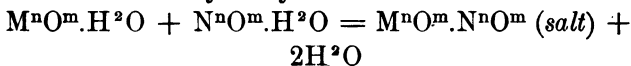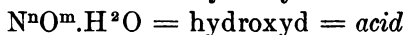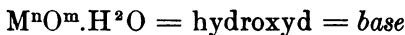
The three conceptions are fundamental in chemistry. Base, acid, salt. Yet neither base nor acid is to be understood in the absolute sense. Two metallic hydroxyds may act as base and acid towards each other, or in other words one is more basic than another. We shall find examples as we proceed. This much, however, impress upon your mind: An oxyd is rarely an active agent; in order to make one oxyd act upon another oxyd strong external impulse is needed, such impulses being heat and electricity. The internal activity becomes manifest towards the surroundings with the formation of the hydroxyd. This will become clearer in the next chapter.

Allow a portion of the liquid, in which you have saturated the lime hydroxyd with the sulfuric acid, to evaporate on a watch crystal. Groups of crystals will be formed, colorless, needle-shaped. Examine them with a microscope. They are often stellar, that is, radiating from a centre. When heated these crystals will loose water readily; they are $CaO.SO^3 + 2H^2O$—a vitriol in which two molecules of loosely-bound water of crystallization are tacked on to the salt proper as in iron vitriol and copper vitriol.

Action of the lime gas upon the lime hydroxyd.— Lime water is the $\frac{1}{10}$ per cent. solution of the lime or calcium hydroxyd in water. Generate the gas as above and let it bubble through some of the solution in a test-tube; a turbidity appears at once which gradually turns to a milky white color and white

sediment. Filter this upon a small paper filter,
dry it. It has no taste. Heat some of it to yellow
heat upon a bit of sheet-iron (platinum preferable
but too costly); after cooling transfer it to a slip of
reddened litmus paper and moisten with one drop
of water. Observe that it slakes and the litmus
turns blue under the white mass. Place another
minute quantity of dry precipitate upon a watch
glass or plain glass slide and examine, after moisten-
ing it, with a high power of the microscope. Minute
but perfect transparent rhombohedrons appear.
Hence deduction : *Lime gas converts lime hydroxyd
into calcite* from which we started. High heat
breaks up the combination of the two oxyds ; at low
heat (temperature of room) they recombine. Con-
clusion : Very high heat always counteracts the
chemical attraction, tends to separate the minute
mass-units. Now let the lime gas bubble through
another portion of the lime water and leave it for
some time, being called away. On returning we find
the original milkiness all gone ; evidently the calcite
has been dissolved in an excess of gas. Boil the clear
solution and shortly milkiness as well as sediment
reappears. Conclusion : Boiling heat expells the
solving excess of gas, the dissolved calcite being it-
self almost insoluble (one part in 250,000 parts
water), must precipitate. This is the reason why the
hard water of limestone regions always gives a sedi-
ment after boiling and the boiled water becomes
soft. Here is some lime water which has been
standing for quite a while in the open beaker glass.

Note that a film has been forming on the surface. The film shows *iridescence* in strong sunlight. Remove some to a glass slide and you will find with a high power the identical rhombohedrons. Deduction : *If calcite forms under these conditions it is evident that the lime gas must be part of the atmosphere.* And since the film forms much more rapidly in a crowded room than outside, we must reason that lime gas forms part of the effluvia or gaseous emanations of the human body. Another important side-gain is that the hardening of *mortar* must be owing to the absorption by the slaked lime of the lime gas in the air. Mortar is a mixture of 80 to 85 parts of sharp sand with 20 to 15 parts of quick-lime in the slaked condition.

All the actions observed are identical for calcite, crystalline limestone and common limestone ; their substance is identical, though their look is very different. This must be noticed, however, that the gas evolved from common limestone possesses a fetid odor which is owing to oily matter often contained in the limestone.

Summary of limestone lesson. Discovery of a gaseous oxyd whose non-metal Y is at present unknown. Of a metallic oxyd (probably) whose action towards the acids is equal to the oxyds of iron and copper, though we do not know the metal contained therein. The oxyd differs by its tendency to form hydroxyd and by its action on litmus paper, which we call *basic* action.

CHAPTER V.

THE LESSON OF WOOD ASHES.

WE have before us the familiar and homely material—ashes. There are evidently two kinds. For in the one we find fragments of partly coaled wood, and in the other hard, glassy nodules known as clinkers. The first is the remnant from burning wood, the second the remnant from burning coal in a kitchen range. Why should I bring these materials before you? They look unpromising enough. Because I find, upon trial, that the wood ashes produce a strong, biting taste similar to that of slaked lime, whereas the coal ashes show no taste whatever. There must be something in the wood ashes outside of the ordinary earth calling for investigation. The Roman historians tell us that when their armies came in contact with the Teutonic tribes on the Rhine, they found it a custom among these for the women to do up their hair with a kind of ointment, and this they made up from fat and wood ashes. It was indeed what later on was called *soft soap*. Whilst these people were at that time, 2,000 years ago, barbarians much like the American Indians, they had the spirit of investigation stalking among them, and this spirit is stalking among them now. When linen and woolen

cloths had superseded the skins of animals, the original hair ointment was found to possess excellent cleansing properties; the manufacture of soap became a separate trade, and wood ashes came to be an article of commerce. The early pioneer in America, for many years, had nothing to exchange for groceries and other store goods but the ashes which he collected from burning out his clearings in the forest. However, the valuable part of wood ashes is only about 30 per cent.; the storekeeper had no use for the 70 per cent. of waste. The farmers were made to extract the valuable portion with hot water, to strain the liquid through canvas, to boil down the liquid to solidity, in iron kettles or *pots*, hence the commercial product came to be called *potash*. This material is not yet pure; it is of brown color, and contains other soluble parts of the ashes. It undergoes a refining process, becomes white, and goes under the name of *pearl-ash*. However, wood has become so scarce everywhere that it can no longer be burnt for the sake of the ashes. How means were found to replace it successfully, in more recent times, we shall see in a following chapter.

Investigation. We have boiled down the liquid— the *lye*, " lie " (pronounce lee) in French, " lauge " in German. In Germany potash was called " laugensalz "—salt made from the lye.

First let us see how the potash acts at high heat. We place some in a hard-glass tube closed at one end. First some water condenses in the upper tube.

At red heat the substance becomes liquid, and then
we observe small gas bubbles arising from the con-
tact between the liquid and the glass, the mo-
bility is changed to sluggish flow.   Question:
Have the escape of gas bubbles and change of flow
anything to do with an action upon the glass? or
is it inherent in the potash itself?   To answer, let
the glass tube be substituted by a metallic vessel,
say an iron crucible.   The potash melts as before
but no bubbles come; the liquidity remains the
same.   It follows that escape of gas is caused by in-
teraction or reaction upon the glass.   Potash is fusi-
ble at red heat unchanged : remember this important
fact.

Act with sulfuric acid or acetic acid upon the
dry potash and upon its solution in water.   In
either case there is strong effervescence.   We apply
the same procedure to the examination of the gas
which we used with the lime gas.   We find the gas
in all its actions like the lime gas.   Moreover, a
white granular salt falls out when sulfuric acid de-
composes the potash, a vitriol.   Therefore we will
be justified in the assumption that potash is com-
posed of two oxyds :

$$PO.Y^nO^m$$

in which P as the first letter of potash, stands for a
metal as yet unknown to us, because its vitriol is
unlike the known vitriols in its crystal form,
unlike also as to solubility, and especially unlike in
this, that heat does not break it up; the vitriol
$PO.SO^3$ stands the heat of the blast-lamp, as I here

show you in the glass tube. The vitriol is more like the lime vitriol than like the iron and copper vitriols; since the action of potash and lime hydroxyd are both *basic* to litmus. Since heat neither breaks up the potash nor the potash vitriol, how shall we get at the hypothetical oxyd PO? Let us reason: We found calcite insoluble, but convertible into oxyd. Suppose we bring the solution of potash together with the lime oxyd in this test-tube, and let this be represented by the scheme:

$$PO.Y^nO^m + CaO + \text{water.}$$
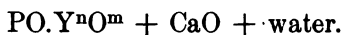
CaO will become slaked lime with the water, we will then get

$$PO.Y^nO^m + CaO.H^2O + \text{water} + \text{boiling heat.}$$
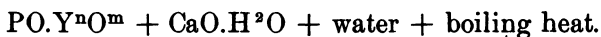
We notice turbidity at once, then flocculency, then a granular precipitate. We filter. The filtrate with sulfuric acid does *not* give gas, but a granular salt falls out slowly as the liquid cools. The action must, therefore, have been

$$PO.Y^nO^m + CaO.H^2O + \text{water} + \text{heat} = CaO.Y^nO^m + PO.H^2O + \text{water}$$
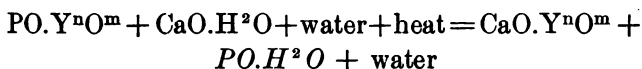
the non-metallic oxyd Y^nO^m has gone to the lime, and only the hydroxyd $PO.H^2O$ remains in solution. The filtrate causes deeper action on the skin of the fingers, on litmus paper and on the tongue. It also follows that $PO.H^2O$ is much more soluble in water than $CaO.H^2O$.

Potassium hydroxyd, caustic potash, caustic potassa, potassium hydrate. The first of these names I want you to use. The second and third names are older

and still used in the drug trade ; the third name was the current scientific name and is used by the majority at present. But I want it to apply to a separate conception. To make myself clearly understood we will return to the action of water upon oil of vitriol. Represented symbolically we have there to start with :

$$H^2O.SO^3.nSO^3.$$

Adding water, little by little, there is much heat, also hissing noise, this lasting until the nSO^3 have combined with nH^2O and we have now only

$$H^2O.SO^3$$

our concentrated sulfuric acid—the true hydroxyd. But when you add to this more water, both being at ordinary temperature—the liquid warms up and can even reach boiling heat. This heat means *more chemical union* and may be scheduled

1st hydrate $H^2O.SO^3.H^2O$
2d hydrate $H^2O.SO^3.2H^2O$
3d hydrate $H^2O.SO^3.3H^2O$

.   .   .   .   .   .

nth hydrate $H^2O.SO^3.nH^2O$

and similarly :

$$H^2O.PO = \text{hydroxyd}$$
1st hydrate $H^2O.PO.H^2O$
2d hydrate $H^2O.PO.2H^2O$

.   .   .   .   .   .

nth hydrate $H^2O.PO.nH^2O$
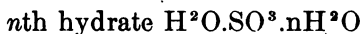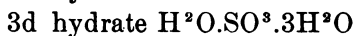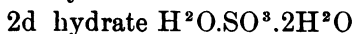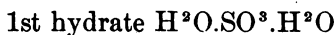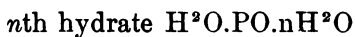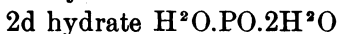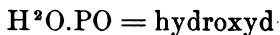
The nth hydrate may be, in fact, what we would

otherwise designate a *dilute water solution* of the hy-droxyd. Returning to the matter immediately before us, we evaporate the water solution of $H^2O.PO$ to dryness in an iron, copper or silver dish. Glass and porcelain are strongly attacked. Prove this statement by using a small beaker glass and a porcelain crucible; they are not destroyed but lose the lustrous surface and some of their material enters the liquid. After the mass has become dry at boiling-point of water, heat over an open flame. Soon fluidity will occur, more steam will be given off; at red heat white vapors appear and, using a small portion, it will slowly disappear: the hydroxyd is *volatile* at red heat. But how do we know that this material is hydroxyd still; why is it not the oxyd, when the lime hydroxyd looses its water so readily at red heat? Revolving in our minds all the actions heretofore performed, we remember that both iron and zinc decompose water at red heat; it may even do so when the water is united strongly to another oxyd. The rig will be simple. A short piece of hard-glass, thick-walled tubing closed at one end; a perforated stopper, a narrow tube drawn into a fine opening and inserted into the stopper will probably suffice. We introduce a piece of the problematic hydroxyd with some zinc shav-ings, insert the stopper, hold the tube by means of a clamp in inclined position and apply heat. With the melting of the hydroxyd, gas bubbles appear, and ere long the mass will want to froth out of the tube, the escaping gas burns, the flame deposits

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drops of water against a cold dish—the gas is hydrogen. In symbols the action is

$$PO.H^2O + Zn + heat = PO.ZnO + H^2.$$

After cooling we find that the mass is quite soluble in water, all but some remaining zinc chips. Here is one example of two metallic oxyds combining to form a salt, because one, PO, is more basic than the other, ZnO. Thus, whilst proving the hydroxyd, we have incidentally discovered that this latter is a most powerful agent, rivalling the sulfur hydroxyd. It corrodes the skin rapidly; it destroys paper and sawdust; it dissolves wool and hair, horn chips and many other bodies. In these actions many interesting and useful new substances are formed, some of which we will inquire into hereafter. We find ourselves now in possession of the two most powerful agents $H^2O.SO^3$ and $PO.H^2O$. Acting upon each other they produce the neutral vitriol $PO.SO^3$ and water. Acting separately, they lend us their latent power.

Action of calcite, of potash, of lime hydroxyd, of potassium hydroxyd and their hydrates upon the water-soluble vitriols of iron, zinc, copper. The vitriols are in dilute solution $(\frac{1}{100})$.

1. $CaO.Y^nO^m + CuO.SO^3$ + boiling heat, escape of gas, green precipitate.

   + $FeO.SO^3$, slight brownish precipitate.

   + $ZnO.SO^3$, no precipitate.

2. $PO.Y^nO^m$ + $CuO.SO^3$, at ord. temp. blue precip., at boiling turns black.

+ $FeO.SO^3$, at ord. temp. light precip., at boiling turns dark.

+ $ZnO.SO^3$, at ord. temp. white precip., at boiling remains white.

3. $CaO.H^2O$ + $CuO.SO^3$, precipitate at ord. temp. and complete at boiling heat.

+ $FeO.SO^3$, precipitate at ord. temp. and complete at boiling heat.

+ $ZnO.SO^3$, precipitate at ord. temp. and complete at boiling heat.

4. $PO.H^2O$ + $CuO.SO^3$, first blue precipitate which turns black.

+ $FeO.SO^3$, light green precipitate which turns black.

+ $ZnO.SO^3$, white precipitate which dissolves in excess.

It can easily be proved that the precipitates formed under (2) are the combinations of CuO, FeO, ZnO with Y^nO^m, whilst the PO combines with SO^3. $CuO.Y^nO^m$ turns black on boiling, because the CuO is not very basic and cannot hold on to the non-metallic oxyd when the shattering power of heat-waves pounds upon the compound. The same is to be said about $CuO.H^2O$ under (4) the CuO cannot hold on to the H^2O. The white precipitate (4) in zinc solution—$ZnO.H^2O$ dissolves in excess of the agent because the soluble salt $PO.ZnO$ forms, thus

First : $ZnO.SO^3 + PO.H^2O = ZnO.H^2O + PO.SO^3$.

Second : $ZnO.H^2O + PO.H^2O = PO.ZnO + 2H^2O$.

Of iron there are two vitriols—a green and a yellow, the latter produced by acting upon iron with the hydroxyd $H^2O.SO^3$ when SO^2 escapes instead of hydrogen.

The green vitriol contains the oxyd FeO, the yellow vitriol contains the oxyd Fe^2O^3. The two vitriols act differently on our four agents. But the one important action is that of *calcite* for $FeO.SO^3 +$ water $+ CaO.Y^nO^m =$ no precipitate.

$Fe^2O^3.3SO^3 +$ water $+ CaO.Y^nO^m =$ brown precipitate, the action being slow at ordinary temperatures, rapid when heat is applied. Hence we have here a means of separation for the two oxyds of the same metal. (Details for this in the Chemistry of the Metals.) Likewise if the vitriols of Cu, Fe, Zn were mixed together (the iron vitriol being of the green kind), we would be able to separate the oxyds—for (Cu and Zn) vitriols precipitate by calcite or chalk and heat, separating the iron. The precipitate boiled with $PO.H^2O$ will leave the CuO as a solid and take the ZnO in solution. Our wealth is increasing as we go along.

The metal potassium. Having seen that the oxyd PO is not obtainable, but only the hydroxyd $H^2O.PO$, and that this latter is quite volatile, their remains only one raw material, the potash. Though it be a salt, the peculiar nature of its non-metallic oxyd makes it possible to be broken up by coal, at a white heat. Cut a piece of ¾″ or 1″ gas pipe P (Fig. 31) six inches long, fit on a cap C, an elbow E and a pipe R of same length, all joined by thread.

Fill *P* with a mixture of charcoal-coated iron chips, 30 grams of fused potash, 10 grams of burnt lime. Screw on *E* and *R* and set into furnace *F*. The latter is heated with gasoline burner *B*, but a good wind furnace and coke will give a suitable heat also. In order to prevent the pipe from burning through, it is well to coat it over with several coats of *charmotte* or *braise*, a mixture of three parts of ground brick and one part of fat fire-clay. The pipe *R*

FIG. 31.
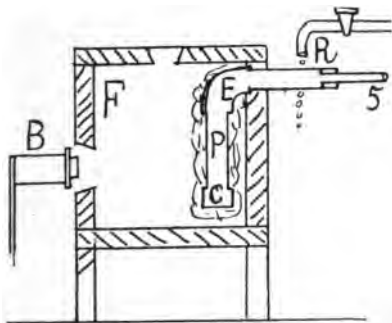
is kept cool by a wrapping of blotting paper upon which water drops from the hydrant or spigot. A cork stopper 5 with glass tube permits the gases to escape. The burnt lime was added to the charge to make the potash less fusible; the iron to hold the charcoal down, preventing it from floating to the top. This charcoal-coated iron is made by heating iron chips and sugar together in a covered crucible until no more gases escape. After yellow heat has been reached, combustible gas will appear and burn

at 5 with either a purplish or yellow flame.   Keep up
the fire for an hour, then cool down.   A gray and
black loose mass will be found in R.   If some be
thrown into water a hissing will be heard and for a
short time a fine purple flame.   The black material
is a mixture of small metallic pellets and a spongy
substance.   By returning this mass to a smaller
apparatus, of exactly the same form, the metal can
be distilled from the sponge and appears then almost
pure in R.   The electric current also decomposes the
hydroxyd $PO.H^2O$ thus : The metal deposits on the

FIG. 32.
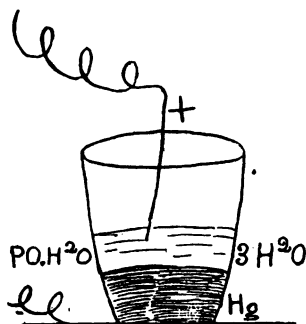
negative pole (cathode) whilst hydrogen forms at the
same pole and oxygen escapes at the positive pole.

$$PO.H^2O + current = P + H^2, + O^2$$
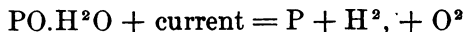
It is difficult to keep the metal from burning up
again in presence of the oxygen surrounding it.
The difficulty may be avoided by pouring some
mercury into the crucible (Fig. 32) and some of the
third potassium hydrate over it.   If now the cruci-

ble be made the negative pole and the positive pole
be a platinum wire, the metal potassium in the
moment of liberation combines with the mercury,
alloys with it, and thus is kept from the air. The
product is the potassium amalgam Hg^nP^m. We
place the latter in a small glass retort and distill
off the mercury at 300° C. Potassium remains as a
liquid. At a red heat it also becomes volatile and
will fill the flask as a fine green vapor. The retort
must be kept filled with hydrogen to keep out the
oxygen of the air.

Physical properties of the metal. Potassium has
a silver-white color, strong metallic lustre. But in
presence of air tarnishes at once, becoming covered
with a gray film. Therefore, the metal must be kept
under a liquid which does not contain oxygen—such
as kerosene. The metal is soft, like fresh putty at or-
dinary temperature, becomes brittle below the freez-
ing point; that means it crystallizes, appearing in
tetragonal pyramids. It melts at 62.5° C.; at red
heat, 730° C., the liquid boils like water; the vapor
is green. Its specific gravity is 0.865 (water 1),
hence, it floats on water, but sinks in kerosene, sp.
gr. 0.76 — 0.78. The specific heat or heat capacity
is 0.166 (water = 1).

Chemical properties. Potassium decomposes water
with great energy, because of all metals it has the
strongest affinity for oxygen.

$$P + H^2O = PO + H^2$$
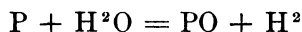
but since an attraction exists between the oxyd and
the water the action really is

$$P + 2H^2O = PO.H^2O + H^2.$$
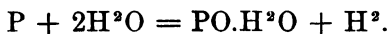
For instance, if you wish to ignite coal-oil which floats on water, you would just throw a piece of potassium on the water, and the oil would be on fire at once.

I said potassium had the strongest attraction for oxygen of any metal. Why, then, were we able to dislodge it by iron and by charcoal? The answer is found in that potassium is so easily *volatilized.* We could not separate the calcium from the lime oxyd, because the calcium is *not volatile.*

Proof of the nature of the unknown Y in lime gas. Once in possession of potassium, we will try it upon the lime gas, which zinc only changed into combustible gas (see above), and of which we remained

Fig. 33.
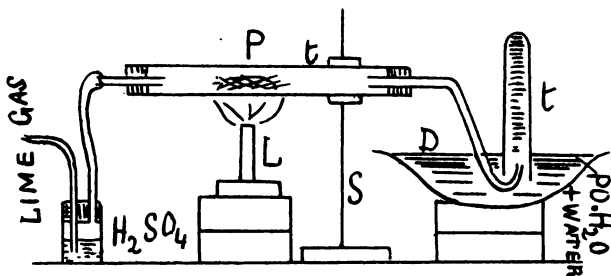
doubtful whether it was Y or a lower oxyd of Y. Let the lime gas be generated from calcite, chalk, or limestone by means of the acetic acid as before. Let the gas bubble slowly through $H^2O.SO^3$, Fig. 33, thence pass it into the combustion-tube t, in

which a piece of potassium has been placed at P.
If the dish D contains the 6th potassium hydrate,
as also the test-tube t, then there will be perfect
absorption of the gas as soon as all the air is ex-
pelled from the apparatus ; because we know that
the potassium hydroxyd as well as the different
hydrates, absorbs the gas energetically in order to
become potash $PO.Y^nO^m$. Now let the potassium be
heated with the lamp L.   It melts, spreading over
the glass and forming a perfect metallic mirror.
Then it ignites and burns with the characteristic
purple flame almost the same as in air, a white
smoke developing.   Soon the potassium becomes
incrusted with a white material and a black
material.   All the gas becomes absorbed for a while,
then reappears in the tube t.   This designates the
end of the action.   After cooling, we remove the
mass from the tube.   The white portion gives all
the actions of potash : Strong, bitter taste, easily
soluble in water, and gas evolution with acid.   The
black portion is not soluble in water ; we separate it
by filtration.   It looks like lamp-black or soot.
Under the microscope we find it to be of brown color
and translucent with yellow or brown color.   At
red heat it burns and disappears.   If the burning
be done in an open tube, one end leading by rubber
tube into lime water, Fig. 34, and air being sucked
through by means of an *aspirator*, then the lime
water will become milky ; the white sediment being
rhombohedrons.   Hence we deduce that the black
substance is the Y in the lime-gas, because from it

comes lime-gas by combustion.   Now we have many
times observed that charcoal burns and disappears,
leaving a slight residue of ashes, and we naturally
will ask : Is there a communion between the black
·Y and charcoal?   To satisfy the query we place a
splinter of charcoal in the tube T, and fresh lime
water in the test-tube.   As the charcoal burns, the
lime water becomes milky with calcite.   Hence we

FIG. 34.
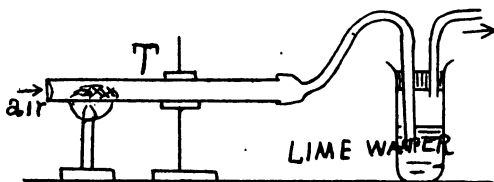
will make the deduction that charcoal is either
wholly or partly made up of the black substance Y,
and we resolve the Y into C, which is the first letter
of the Latin word *carbo*, the equivalent of the Eng-
lish charcoal.   With characteristic inconsequence
the English language makes *carbon* out of carbo.
Our lime-gas becomes now C^nO^m; the calcite becomes
$CaO.C^nO^m$; potash $PO.C^nO^m$, pronounced *calcium car-*
bonate, and *potassium carbonate*.

The symbol for potassium should be P as we
adopted it.   But here again the English chemists
are inconsequent in choosing K, which is the first
letter of the Arab word *kali*, which means " burnt,"
but was given by the Arab chemist Geber to our
potash.   This word was taken up by all chemists

with the Arab prefix " al," *i. e., alkali,* to mean any body which shows the essential action of potash, these actions being called *alkaline* actions. *A solution is said to be " alkaline" when it turns red litmus to blue.* German and Swedish chemists call the metal potassium *kalium,* English, American, and French chemists stick to potassium, but they accept the symbol K.

CHAPTER VI.

THE LESSON OF COMMON SALT.

COMMON salt is before us in three forms. 1.
Rock salt as mined at the mouth of the Mississippi,
in Canada, and other places in America. It is
beautifully transparent; colorless or colored, some-
times intensely blue. It is found as large, perfect
cubic crystals, and again as immense, solid, irregu-
larly shaped masses like ice; or as fine grained,
snow-white or dirty gray, or yellow, or red masses.
It cleaves perfectly in three directions at right
angles—cubical cleavage. It presents slight re-
sistance to the knife or to the drill. It has a
strong taste; is readily dissolved by water. 2. Salt
from evaporation of salt springs and salt wells, in
snow-white cubic crystals, which are all hollow on
the faces. 3. Salt from evaporation of sea-water.
It is certain that all the deposits of salt, found in
nearly all geological formations, were at one time
dissolved in the sea. It is likewise certain that salt
springs and wells dissolve the rock salt they find in
the rocks, so that, in the end, our three kinds of salt
are practically only one kind, *sea-salt.* Man and
animals crave salt, their bodies must have salt or
die. Hence all the languages derived from some
primitive language have nearly the same name for

the substance: Greek: *hal*, Latin: *sal*, French: *sel*, German: *salz*, English: *salt*. The plant-eating animals get some salt with the grass and leaves, but it is known that they will travel 100 miles and more to get a salt spring or salt-lick, to satisfy the craving for salt. Carnivorous animals get their salt in the blood of the grass-eaters on which they prey. Man takes his from both plants and herbivorous animals. Bloody wars have been fought for the possession of a salt spring or salt mountain.

The United States are well supplied with salt, and need not go to the evaporation of sea-water. Germany is very rich in salt; exports much to other less favored nations. Where the sun's heat can be made use of for evaporation, the sea-water gives very cheap salt.

Investigation. Heat does not break up the salt. Holding a piece of salt in the flame we see that it melts quickly and colors the flame a deep orange-yellow. Heating the salt in a glass tube we notice *decrepitation* (enclosed mother liquor escaping explosively), then a slight water condensation, then melting, then boiling and forming of a white sublimate. No odor, nor gas.

The sublimate shows itself made up of cubic crystals, tastes and acts the same as the original salt. Deduction: Salt is volatile without decomposition. It may be a simple body as far as heat action shows. But not so by its behavior towards electricity. We place salt upon a platinum crucible lid, the lid being in contact with a sheet of copper and the

latter forming the positive pole of the current.   As soon as we bring the other pole wire in contact with the salt, the salt melts and an evolution of gas ensues accompanied by a very strong and peculiar odor. The same odor is produced if we mix salt with blue vitriol and heat in closed tube.   But let us try our two strong agents : Sulfur hydroxyd and potassium hydroxyd.

Salt+$KO.H^2O$+heat=no gas, no apparent effect.

Salt+$H^2O.SO^3$+heat=copious evolution of colorless gas possessing a strong, pungent odor, and *reddening* blue litmus.   Let this gas be called *salt-gas*.   We let the gas pass into water : it is absorbed eagerly, the solution becoming warm.   Looking at this phenomenon we cannot deny that it is similar to the action of $H^2O.SO^3$ upon calcite, hence that salt must be composed of two oxyds

$$M^sO.N^sO.$$

in which neither the metal M nor the non-metal N is known to us.   With this supposition as a guiding thread, we proceed with experiments until we shall have established the truth or falsity of the conception, and recognized the properties of both M and N.

Salt gas, spirits of salt.   If our assumption be true, the production of salt gas must occur thus

$$M^sO.N^sO + H^2O.SO^3 = H^2O.N^sO + M^sO.SO^3$$
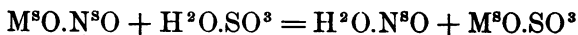
the salt gas must be the hydroxyd of the non-metal oxyd N^sO.   The gas contains *hydrogen*.   For if we expose zinc to it hydrogen is evolved at once.   Let

F be a flask holding about 500 c.c. Let it be fitted
as in Fig. 35, with funnel, stopper and escape tube,
all standing on a tripod so that heat may be applied.
Let C be a bulb tube filled with cotton, to retain
any particles carried over by the gas. T is a hard-
glass tube with two perforated stoppers. B a bulb
tube providing for any liquid mounting back from
D. t is a test-tube to receive any gas which may be

FIG. 35.
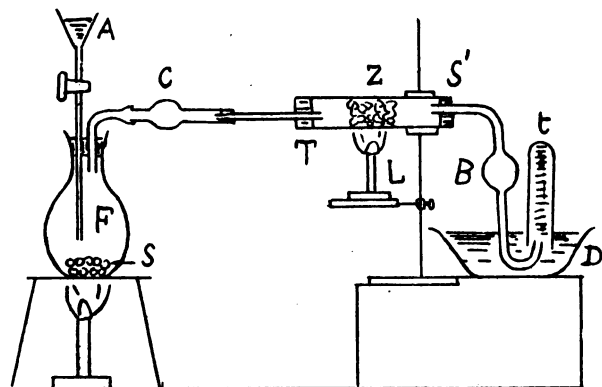
generated. Remove stopper S', introduce 50 grams of
salt into F at S, fill funnel with $H^2O.SO^3$ and drop
the latter slowly into F for some time, until upon
·adjusting S' the gas bubbles are all absorbed in the
water in dish D.   Open at S' and introduce zinc at
Z. Close S' and adjust tube t.   The speed of gen-
eration of the gas is to be judged by the frothing of
the salt. T being cold (flame L not having been
lit) at start, will now warm up: zinc decomposes

gas at ordinary temperature, the combination pro-
duces heat. Prove the gas in test-tube is hydrogen
by showing it inflammable. At Z a new body has
been formed which is fusible, proven by means of
lamp L. By withdrawing it from the tube it is found
to be soluble in water. (Prove solution by testing
with potash and also with $KO.H^2O$), therefore this
substance cannot be zinc oxyd for this latter is neither
fusible nor soluble in water; it must be a combination
of zinc with the unknown N. Acting upon it with
$H^2O. SO^3$ the pungent gas forms same as with the
salt. Nevertheless the combination may contain
oxygen. As we know the great avidity of potassium
for oxygen, let us act as follows: We bring into a
test-tube a part of the unknown compound ZnN^8O;
we fill the tube with hydrogen, excluding thus any
air; we then add a piece of bright, carefully cleaned
potassium and apply heat, hydrogen still passing in.
The action would have to be thus:

$$ZnN^8O + 2K + heat = Zn + N^8K + KO$$
$$or = ZnKN^8 + KO$$
$$or \text{ with } 3K = ZnK + N^8K + KO$$
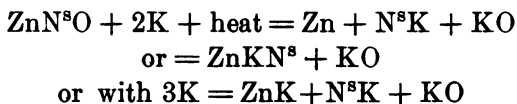
It will evidently not matter which of the reactions
ensues, or whether all three occur at the same time.
The essential point is the forming of KO; because
if water be now brought into contact with the mass,
$H^2O.KO$ will be formed and will cause the change
in litmus from red to blue. The experiment will
give true information only, if ZnN^8O be in excess,
for otherwise K would be left and in contact with

water would give the hydroxyd + hydrogen. The experiment must be made with much judicious care, and will prove that KO is not formed and, hence, that *oxygen is not present* in the compound and therefore not present in the salt gas. Our preliminary supposition was *wrong :* Salt gas must be N^sH. How are we to set free N^s ? In the case of the limestone gas we were successful with potassium because the C (carbon) does not combine with potassium ; but in this instance, when we find the unknown N^s to combine with zinc, it seems more than likely that it will combine with potassium also. However, let the trial be made. The apparatus, Fig. 35, will be quite suitable. We simply substitute a piece of potassium at Z in place of zinc. We note a strong action even at ordinary temperature, a white substance forming and hydrogen evolving. The white substance forms cubes and octahedrons, it tastes like common salt ; hence we conclude that the metal M in salt must be similar in its nature to K. Whilst this is welcome information, it is not what we are looking for. The unknown *is not set free.*

Another train of thought is needed ; we know the unknown to be a hydrogen combination. Now the metals having failed us, let us try the non-metals. Of these we know oxygen, azote and sulfur, and of these oxygen seems the most active. We reason along the scheme

$$2N^sH + O = 2N^s + H^2O$$
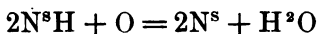
Mixing oxygen and salt gas at ordinary tempera-

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ture has no effect as seen in this cylinder, which
holds the mixture; therefore let the mixture, one
volume of each, be passed through the glass tube *T*
(Fig. 36) and let asbestus *A* (mineral wool) partly
fill the tube. The asbestus being brought up to
redness, the gas mixture slowly passes through it
in measure as the cylinder *C'* is raised and the
cylinder *C''* is lowered. While *C* fills with mercury
the pipette *P* fills with a gas of pale-green color.

FIG. 36.
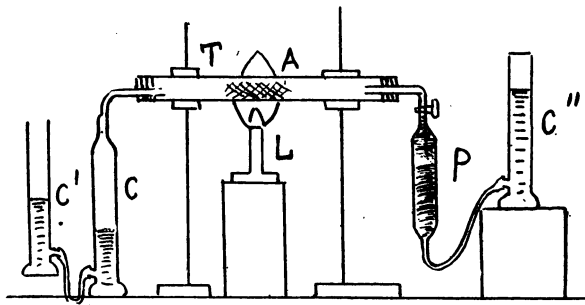
This gas we shall hereafter name *chlorine*, (*Cl*.) from
Greek chloros = green. For consistency's sake the
name should be chlorium—as hydrogenium, ferrum,
stannum, potassium. (The great chemist, Berzelius,
never gave up his belief that this chlorine was a
compound and not an element, that it does contain
oxygen, but that we are not able to separate the
two. The demonstration we have gone through
above leaves very little doubt that the salt gas and
hence chlorine do not contain oxygen.)

Chlorine, physical properties. A green gas of

peculiar, very strong odor; offensive to the mucus membrane, producing ulceration upon the latter down into the bronchial tubes and capillaries of the lungs, painful coughing; must be careful not to breathe the gas; if necessity compels to stay in a place filled partly with chlorine must keep mouth and nose covered with a wet sponge.   The gas is very heavy.   It is 35.5 times heavier than hydrogen, 2.45 times heavier than air, and 2.216 times heavier than oxygen.   One litre of the gas at 0° C. and 760 mm. mercury pressure weighs 3.178 grams. 1 c.c. equals 0.003178 grams, roundly 3 milligrams. The gas dissolves somewhat in water.   The maximum solubility lies at 9.5° C., and corresponds to 2.75 times the volume of the water.   Hence 10 c.c. of water will absorb at best 27.5 c.c. of the gas. But since 1 c.c. of gas weighs three milligrams, the 27.5 c.c. will weigh 82.5 milligrams, or 0.0825 grams, and hence in weight per cent. 0.825.   It is well to remember that the most concentrated water solution of chlorine does not contain quite one per cent. of chlorine; at 30° C. only 1.75 volumes equals 0.525 weight per cent.   At boiling heat the chlorine is *completely* driven from its solution.

Chlorine gas condenses into a mobile yellow liquid under a pressure of 8.5 atmospheres (127.5 pounds per square inch).

Preparation of chlorine.   In the practical preparation of chlorine it is more advantageous to supply the oxygen in combined form, as a superoxyd, an oxyd which contains more oxygen than it can hold

firmly.   Nature furnishes us with such in the so-called soft *manganese ore* MnO², the *pyrolusite* of mineralogists.   The salt-gas acts upon this oxyd even at ordinary temperature ; very energetically at about 60° C.; thus

$$MnO^2 + 4HCl \text{ (salt-gas)} + heat = MnCl^2 + 2H^2O + 2Cl.$$
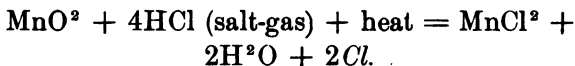
Only one-half of the chlorine contained in the salt-gas appears as *free chlorine*, the other half forming, with the metal manganese, a pale, rose-colored salt —manganese *chlorid*, MnCl².

Neither is it convenient nor economical to act with the salt-gas upon the superoxyd.   A solution of the gas in water is much better adapted to this purpose, the best concentration is 20 per cent.   How to make such a solution will be explained in the next paragraph below.   The most suitable apparatus is the Koenig generator, represented in Fig. 37.   *G* is the generating tube drawn out at lower end *0*, where a stout rubber tube *R* is wired onto it.   The tube *R* has at its other end a bent glass spout *P*, which rests upon the edge of the waste vessel *W*. The upper end of *G* is somewhat restricted, and a glass stopper *S* is ground into the restriction.   This stopper is fused to the funnel tube *F*, the latter carries a stop-cock and a receiving bowl for the salt-gas solution.   *L* is the outlet for the chlorine.   *J* is a wider glass tube, fused onto *G*, so as to form a complete jacket around the latter.   The tubulature *E* serves to fill this jacket either in part or entirely

Fɪɢ. 37.
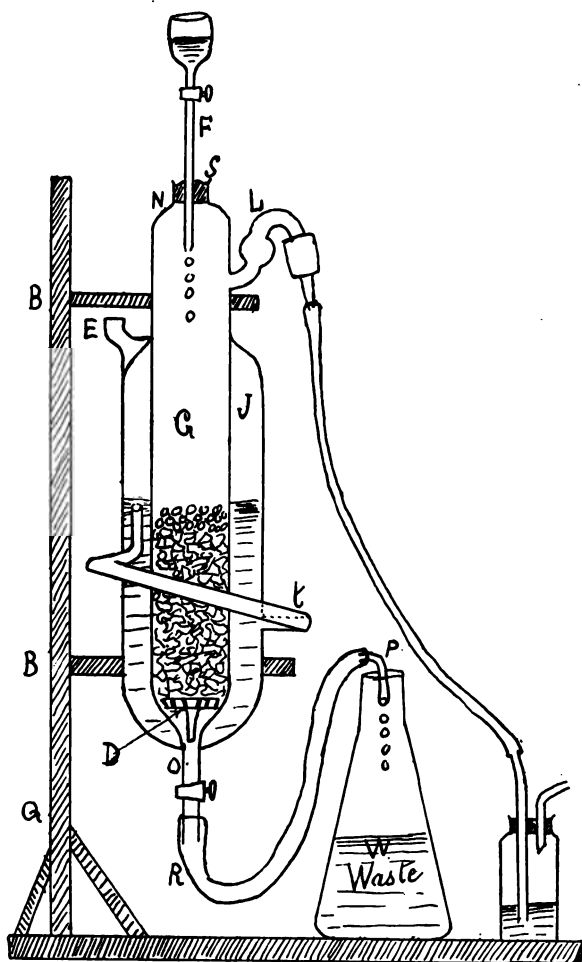
KOENIG'S GENERATOR.

with water whilst a glass tube T encircles the jacket
obliquely, and is fused into the jacket at both ends.
This small encircling tube is full of water, and, be-
ing heated by the small flame from a glass tube or
a Bunsen burner, brings up a circulation and raises
the temperature in J to any desired point.   Upon
the porcelain false bottom D rests the manganese
superoxyd in small pieces, about pea-size.   The
column of MnO^2 should not be over 3 inches high.
The apparatus is held by the brackets B, B, B,
against the wooden stand Q, the latter being sup-
ported by the bottom plate N.   We start by filling
water into G until the tube R is full and the water-
level in the spout P is even with the level at the
false bottom D.   Then we heat the jacket to 60° C.,
and thereupon drop the salt-gas solution at the rate
of one drop a second.   There will then be a steady
current of chlorine gas issuing through, whilst an
equally constant discharge of the by-product, $i.$ $e.$,
$MnCl^2$ will discharge itself at P into the waste
vessel W, provided the bowl of the funnel is kept re-
plenished.   If a stopping be desirable, simply turn
the stop-cock in F.   The gas will not be quite pure.
It will be mixed with some liquid particles and also
with some salt-gas.   Hence we conduct it through
a wash bottle containing some water, then through
another such containing $H^2O.SO^3$; in the latter the
aqueous vapor will be removed, in the former the
other admixtures.   Of course, whenever *dry* gas is
not required, the second wash bottle may be omitted.
You will take notice that the rubber tube R forms

a trap against the escape of the gas downward, whilst the narrow funnel tube keeps the gas from escaping upwards.   But it stands to reason that if a resistance be placed at L of greater weight than the column of liquid in either F or R, then the gas escapes through them, they forming the natural safety valve.

A generator may be rigged more simply and

Fig. 38.
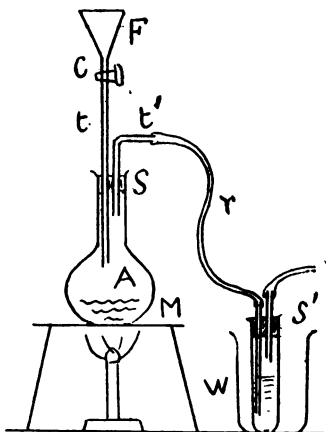
cheaply. A, Fig. 38, is a small flask, t is a glass tube, F a funnel connected with t by a short rubber tube and clamp C, t' tube for escaping gas; r a $\frac{1}{8}''$ rubber tube, W a beaker glass in which stands a large test-tube fitted with rubber stopper S', and partly filled either with water or with $H^2O.SO^3$ serving as wash bottle.   The manganese superoxyd is placed in A at M, F is filled with salt-

gas solution.   The apparatus is ready for use.   In a measure, however, as $MnCl^2$ accumulates in *A*, the evolution of chlorine becomes slower, a steady stream cannot be maintained by it, except for a very short time.   I worked for twenty-five years with such an apparatus, until I made the more perfect one described above.

Chemical properties of chlorine.   Chlorine is a most powerful agent at ordinary temperature, when oxygen is almost inert.   It attacks *all* the metals, and in presence of water dissolves most of them : Gold, platinum, tin, copper, iron, zinc, but not so lead, silver, mercury.

Upon oxyds, it acts thus :

$$CuO + 2Cl + heat = CuCl^2 + O$$
$$MnO^2 + 2Cl + heat = MnCl^2 + 2O$$

Chlorine acts upon all coloring matters taken from plants, such as litmus, indigo, the red cabbage, and many others, in such a way that the color vanishes, *bleaches.*

Upon the hydroxyds of potassium and calcium, chlorine acts as follows :

$$2CaO.H^2O + 4Cl + water = CaCl^2 + CaO.Cl^2O + 2H^2O.$$
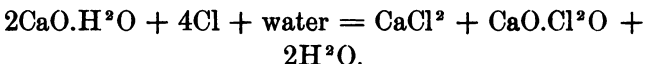
The milk of lime becomes dissolved to a clear liquid.   If the dry slaked lime—flour of lime—be exposed to chlorine the same action takes place, but the resulting product is a slightly pasty solid, and is called *bleaching lime ;* is soluble in water, and is used in large quantities by the bleachers and dyers

of yarn and cloth. The compound $CaCl^2$ does not bleach, only the compound $CaO.Cl^2O$, and in this only the oxyd Cl^2O is the bleaching factor.

Upon potassium hydrate the action is parallel, thus:

$$2K^xO.H^2O + 3Cl = KCl + K^xO.Cl^2O + 2H^2O.$$
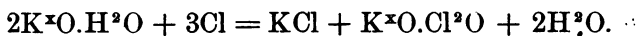
You pass the chlorine gas into the solution so long as it is freely absorbed. The result is a *bleaching* solution. But if we boil this solution for some time, it begins to throw out scaly crystals, white or colorless. Let these crystals be separated from the liquid, then dried, and then heated in a closed glass tube, when they will be seen to melt easily with strong evolution of gas. The gas proves to be *pure oxygen.* (Explode it with 2 volumes of hydrogen.) When no more gas is given out the residue contains only potassium and chlorine, is KCl. The crystals themselves are produced from the boiling solution by the following reaction:

$$6K^xO + 6Cl + water + boiling\ heat = 4KCl + K^xO.Cl^2O^5,$$
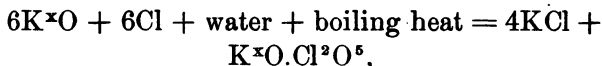
and when the crystals are decomposed by heat:

$$K^xO.Cl^2O^5 + heat = 2KCl + O^6.$$

The crystals represent a compound of the metallic oxyd K^xO with the non-metallic *superoxyd* Cl^2O^5. The latter is unstable, overloaded, hence heat breaks it up easily, and as we have seen above that chlorine drives oxygen from the oxyds, the final result must be KCl + 6 oxygen. The crystals shall be known as *potassium chlorate.* It is a very valuable compound

to us, because we can obtain by it at any time
quantities of the purest oxygen.

Manufacturing process for potassium chlorate. The
potassium hydrate is relatively costly, the cal-
cium hydroxyd very cheap, KCl is also cheap (a
natural mineral *sylvite*). On passing chlorine gas
into water in which have been slaked 3 equiva-
lents of calcium oxyd (burnt lime) at boiling heat
until the liquid has become clear, we have a solu-
tion of calcium chlorate (easily soluble). We bring
into it one equivalent of KCl and potassium chlorate
falls out in crystals (because it is *not* readily soluble
in water).

Composition of salt gas. We found the gas com-
posed of hydrogen and chlorine. Now we have to es-
tablish their ratio in the compound. If we pass one
volume of salt gas over heated zinc repeatedly, in the
apparatus Fig. 36, we find that the volume of the gas
becomes reduced to one-half. Chlorine unites with
zinc, becomes solid so to speak, the remainder is pure
hydrogen. Hence we deduce : Salt gas is composed
of equal volumes of hydrogen and chlorine ex-
pressed by the symbol HCl. If we fill into a cylinder
one volume of hydrogen and one volume of chlor-
ine and let the mixture stand in the diffused day-
light for some days, the volume does not change,
but the two gases shall have become united to HCl.
We can prove this by introducing a few c.c. of
water ; the gas is all absorbed by the water ;
chlorine would have only been slightly absorbed,
hydrogen not at all, Should we expose the mixture

of H + Cl to the *direct* sunlight, the union would follow at once with explosive energy.   It is important to note that the volume of the compound is equal to the sum of the volumes of the components; neither contraction nor expansion taking place. *This is a law for all unions of gaseous bodies in equal volumes.* The name for the compound HCl shall be *hydrogen chlorid,* and all combinations of metals with chlorine shall be named *chlorids,* as we name the oxygen compounds *oxyds.*   Some chemists speak and write *chlorides, oxides;* it is quite immaterial which you use, but choosing one you should stick to it; the shorter sound would seem to be preferable.

Properties of hydrogen chlorid : A colorless gas at ordinary temperature, powerfully pungent odor, exciting the mucous membrane.   Near the freezing-point of water at + 4.4° C. the gas becomes a liquid under a pressure of 30.67 atmospheres or 460 lbs. per square inch.   At a temperature of —73.3° C. only a pressure of 27 pounds is needed.   Liquid HCl is mobile and colorless, heavier than water. No practical use has been found for it.   The specific gravity of the hydrogen chlorid gas is 1.255 (air = 1) ; 1 c.c. of it weighs 0.00163 gram, just about one-half that of chlorine.   By weight the gas contains 97.26 of chlorine, 2.74 of hydrogen.   1 volume of water can absorb 500 volumes of HCl gas at the freezing-point; at 20° C. (common temperature) water absorbs 440 volumes of the gas.   The absorption of the gas produces heat.   This would lead us to think that there must be a chemical affinity

between HCl and H_2O; that there must be *hy-drates*. In fact it is quite probable that two such exist. For, if a concentrated solution of HCl · in water be heated (a thermometer registering the temperature), it will give out for some time only moist HCl gas. The temperature having risen to 100° C., water passes over with HCl and a very concentrated solution condenses having specific gravity 1.19. As the temperature rises the distillate becomes more watery until the temperature reaches 111° C., at which it remains constant whilst a solution distills over possessing specific gravity 1.104. This solution contains 21 per cent. HCl and 79 per cent. of water, nearly the hydrate $2HCl + 15H_2O$. A second hydrate is $HCl + 6H_2O$.

*Hydrochloric acid—Muriatic acid—*HCl + water. These names are given to the water solution of HCl. We speak of highly concentrated acid, concentrated acid, dilute acid, very dilute acid.

	Sp. gr.	Per cent. HCl
Highest concentrated,	1.200	40.77
Highly concentrated,	1.1802	36.29
Strong acid,	1.151	30.58
Medium,	1.072	14.68
Dilute,	1.042	8.56
Very dilute,	1.006	1.12

Problem : Construct with these data a curve whose ordinates shall be the percentage and the abscissae, the specific gravities.

Preparation and manufacture. Small quantities are made by distillation in glass flasks or glass re-

torts.   On a commercial or manufacturing scale,
cast-iron vessels are used, either cylinders, or else
flat pans standing within a brick furnace.   Cast
iron is not attacked by concentrated sulfuric acid nor
by HCl, but is energetically attacked by a solution
of HCl in water.   Such properties render the iron
vessels fit.   Concentrated sulfuric acid acts violently
upon salt even at ordinary temperature; the mass

FIG. 39.
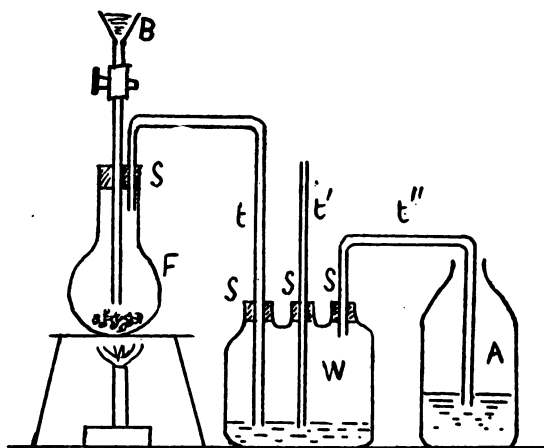
threatens to froth over.   An addition of water gives
relief.   Our prescription is: For every ten grams
of salt take 9.6 c.c. of concentrated $H^2O.SO^3$ and
5.5 c.c. of water.   Mix the two liquids in a beaker-
glass, fill from it the basin B (Fig. 39) of the funnel;
place the salt in the flask F; make connection
with the Wulf bottle W by tube t which passes

under the level of the wash water.   The tube t' also
passes under the surface level and is open at the
top; t' is the safety valve of the apparatus, because
air will pass into it whenever a partial vacuum is
brought about; t'' leads into the absorption flask A
which contains as much water by weight as the salt
taken.   The student takes 50 grams of salt and
places 50 c.c. of water in the absorption bottle.
The stoppers S, S, S must be of rubber.   The flask
F must hold 500 c.c.   All the acid may be put in
at once, and then heat applied gently at first, and
regulated to keep up a steady evolution.   When the
gas stops, finally, the operation is terminated and
you let air in through the funnel tube.   In removing
the flame, it will be seen that the liquid in F solidi-
fies, by degrees, as it cools down.   Remelt it and
pour it out on a clean stone or iron surface.   Let it
be named "crude salt cake."   It must, evidently,
be the vitriol of the unknown metal M, and will be
taken up presently.

Action of hydrochloric acid.   The water solution of
HCl is nearly as powerful an agent as the gas itself,
and for most purposes can be employed in its stead.
Because the metallic chlorids are more readily solu-
ble in water than the vitriols, excepting the chlorids
of silver, lead, and mercury; therefore, we shall use
it in preference to the sulfuric acid, whenever we
desire to dissolve bodies which are not soluble in
water.   As, for instance, we wish to generate lime-
gas.   The calcium vitriol is very insoluble, and we
have heretofore used acetic acid for the decomposi-

tion.   Instead we shall use hydrochloric acid here-
after; the calcium chlorid is much more soluble
than the vitriol, in fact, it will dissolve by merely
allowing it to stand uncovered in ordinary air which
is always more or less moist.   Hence, we can em-
ploy, to advantage, this chlorid in place of concen-
trated sulfuric acid for the drying of gases.   Being a
porous solid, the calcium chlorid offers more surface
to the gas than an equal volume of *liquid* sulfuric
acid.

The chemical actions may be represented thus: If
R stands for a metal, whose chlorid is soluble in
water:

$$R + \text{water} + \text{HCl solution} = \text{RCl solution} + H;$$

and on oxyds

$$RO + \text{water} + 2\text{HCl solution} = RCl^2 \text{ solution} + H^2O;$$

if, however, silver vitriol solution be brought to-
gether with hydrochloric acid, a white, curdy pre-
cipitate falls out at once, *AgCl*,

$$Ag^2O.SO^3 + \text{water} + 2\text{HCl solution} = 2AgCl + H^2O.SO^3 \text{ solution}$$

because the silver chlorid is insoluble in water.
Thus we can prove the presence or absence of silver
in any unknown solution by adding to it a drop of
hydrochloric acid; if a curdy cloudiness follows,
then silver is present.

Pure hydrochloric acid is quite colorless.   The
yellow color of the commercial muriatic acid is
owing to some *iron chlorid* coming from the iron ves-

sels and iron oxyd in the crude salt. The strength of commercial acid is mostly indicated in degrees on the *Beaumé hydrometer*, instead of by the specific gravity. Such an instrument (Fig. 40) is correct if it sinks in pure water at 17° C. to the zero mark. Zero is therefore equal to specific gravity 1.000. In a 15 per cent. solution of common salt (salt = 15, water = 85) the spindle must sink to the mark 15; the degrees being equal divisions. Very concentrated
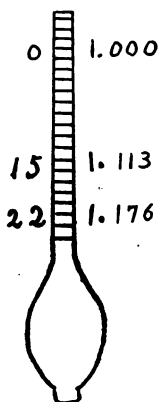
FIG. 40.   FIG. 41.
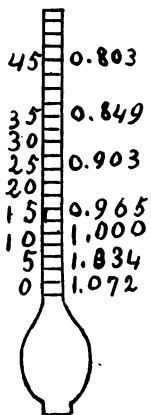
hydrochloric acid is said to be 22° Bé. (specific gravity 1.176). There is, of course, a second spindle for liquids lighter than water. In this instrument (Fig. 41) the zero point is near the bulb, the weight in the bulb, being so chosen that the spindle sinks in a solution of 10 per cent. salt (salt 1, water 9) to the zero point, whilst in pure water it sinks to

division 10; the same unit (found by dividing the space between 0 and 10 into 10 equal parts) is then drawn on the scale upward to the limit of the spindle. Kerosene, gasoline and other coal-oil products are gauged in the United States by degrees Bé. Alcohol is gauged by the hydrometer of *Tralles*. It is not sufficient to say that a liquid stands at so many degrees Bé., it must be said whether reference is had to a liquid lighter or heavier than water, which can be done by the signs +, —, or by letters: l. w; h. w. Thus the light gasoline for gas-making is —87° Bé., and the concentrated sulfuric acid is + 66° Bé. Hydrochloric acid can be shipped only in glass vessels; the sulfuric acid can be transported in iron tanks. The glass vessels—large, spherical, holding 5 to 10 gallons, and being packed with straw into wooden boxes—are known as *carboys*. For manufacture on a large scale get information in Lunge's Manufacture of Soda Ash (recent) or in Ure's Dictionary (old).

Crude salt cake, discovery of the metal sodium. Let some of the crude cake, obtained by action of H_2SO_4 on salt, be heated in a porcelain crucible over an open flame. Dense white fumes are soon seen to arise. The fumes are now diagnosed by us as probably being sulfur trioxyd, oil of vitriol. As the vapors escape, the melting-point of the cake rises. Finally, when no further fumes come off, the stuff appears dry at a red heat. At yellow heat it melts again, and remains so without yielding any more fumes or gas. Reason for the fumes: The

8

crude salt cake is $M^sO.SO^3.H^2O.SO^3$, a so-called acid vitriol, quite constant at low heat, but breaking up at high heat into $M^sO.SO^3 + H^2O + SO^3$. The final remnant is $M^sO.SO^3 =$ salt cake—*refined*. We had added in the recipe given just twice as much sulfuric acid as is needed, and did this knowingly, for otherwise we could not have completely decomposed the salt in a glass flask; the stuff would not have liquefied; the flask probably broken. Salt cake dissolves in cold water easily; this property distinguishes it from the potassium vitriol and the calcium vitriol. In order to isolate the metal let us make use of our experience with charcoal—carbon. We mix the powdered salt cake with powdered charcoal, cover the crucible, and expose it in a charcoal or gasoline furnace to strong red heat. We may do it in a hard glass tube first. Result is a dark-colored mass; metallic particles are not visible, and if we bring it together with water there is no evolution of gas, such as potassium produced. However, it dissolves in water, leaving charcoal powder, which we separate by filtration, and test, after thorough washing, by burning; as it quite disappears (leaving only trace of ash), we are correct in calling it charcoal. The filtered liquid has a brown or red-brown color; it gives alkaline reaction to litmus; has a strong taste. With hydrochloric acid, gives off gas smelling of rotten eggs, and if this gas be passed through a glass tube heated to redness a sublimate of sulfur forms. If bright copper or silver be brought together with the liquid,

the metal turns black, and if these strips of blackened metal be heated in an open tube we get the smell of SO^2. If boiled with finely-divided copper oxyd, the liquid becomes decolorized and does not any more blacken the metallic copper, whilst it' gives still a strong alkaline reaction. From all these observed facts we draw the following deductions:

1. The action of charcoal must have been, symbolically, thus

$$M^sO.SO^3 + nC = M^sS + 4CO + n\text{--}4C;$$

the vitriol was converted into a *sulfid*.

2. The action of metallic copper and metallic silver was probably

$$M^sS + nH^2O + Cu = CuS\,(black) + M^sO.H^2O$$
$$(alkaline) + (n\text{--}1)\,H^2O.$$
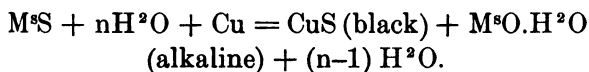
3. The action of copper oxyd was probably

$$M^sS + CuO + nH^2O = CuS + M^sO.H^2O\,(alkaline)$$
$$+ (n\text{--}1)\,H^2O.$$
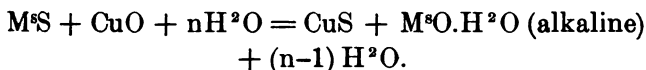
The hydroxyd of the unknown metal is easily soluble in water, and being strongly basic—alkaline—it must be akin to potassium. We evaporate the liquid from (3) to a white solid, which afterwards fuses and then goes off in white fumes, just like potassium hydroxyd. We act upon this material with zinc, and by evolution of hydrogen prove it to be hydroxyd. Next we act upon it with the electric current; gas at positive pole; metallic globules and gas at negative pole; and by using mercury as the negative pole we obtain a solid amalgam, from

which the metal M may be separated by distillation in a current of hydrogen gas.   If we act upon the hydroxyd with charcoal-loaded iron chips at a yellow heat, the metal will distil over, same as potassium, but the flame issuing from the retort burns with a *yellow color* (distinction from potassium, *purple flame*).   In the neck of the retort we find a black mass which acts like that found in the distillation of potassium.   This mass is mixed with the condensed metal.

Properties of the metal sodium.   The name *sodium* is given to the metal by English, French, and American chemists.   Germans and all others give it the name *natrium*, using the first two letters as the symbol, Na, which stands for the chemical unit of mass.   English, Americans, French use the same symbol, hence sodium, Na.   Natrium is derived from Greek *nitron ;* Egyptian and Hebrew *neter*, a name given by those people to the crusts forming around the desert lakelets, and which was found to have similar cleansing properties to potash.   It is now known as soda ash.   Whence the word soda comes is not known, nor what it means.   Perhaps from the Latin *soldere*, English solder, since this material may have been confounded with borax, such mixtures being useful in joining metal pieces by heat.   (Author's notion.)

The metal sodium is soft like wax at ordinary temperature, can be hammered at freezing-point, becomes liquid at about 95° C. (melting-point is higher than that of potassium 65° C.).   In color

it is silver-white like potassium; the fresh-cut sur-
face becomes rapidly dull from oxydation.   Sodium
becomes vapor at red heat, and this vapor has a
purplish color—potassium green.   Specific gravity
at 10° C. is 0.974 (water = 1).   Coefficient of ex-
pansion 0.000073, larger than that of any other
metal except potassium (0.000083).   It conducts
heat and electric waves well, about 37 (silver =
100).   Its specific heat or heat capacity is 0.2934.
Its heat of fusion is 0.73 Cal.

   Chemical properties of the metal sodium.   Thrown
upon water it sets up an evolution of gas and melts
into a globule which is covered by a gray film.
The gas does not ignite, unless the water be heated
to about 60° C., or unless the water be thickened
with gum arabic or glycerine.   We deduce from
this action that sodium has not as much affinity
or attractive tendency for oxygen, as potassium ;
hence less heat is generated.   If the globule be left
on the water until the gas evolution stops, the
globule flattens out suddenly and an explosion en-
sues.   If the globule be taken from water when gas
stops, it is found composed wholly of *oxyd.*   (The
explosion is explained by the sudden rise of steam
when the oxyd becomes hydroxyd.)

   If the metal be heated in oxygen gas, or in a
mixture of air and oxygen, a yellow substance re-
sults which is the *superoxyd of sodium ;* on cooling it
turns white.   It dissolves in water without decom-
position, and can be melted without decomposition.
If heated with copper, lead, zinc or tin the sodium

superoxyd changes these metals into oxyds.   With
HCl it gives $NaCl + H_2O + O$.   If this action be
done in water solution, *oxygen does not escape;* the
water then contains sodium chlorid, NaCl, and hy-
drogen superoxyd (also called peroxyd), H_2O_2 or
HO; we assume therefore that the sodium peroxyd
must have a similar composition to the hydrogen
peroxyd, namely, Na_2O_2, the reaction will be

$$Na_2O_2 + 2HCl + water = 2NaCl + H_2O_2 + water.$$
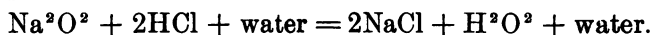
This solution of hydrogen peroxyd is a powerful
oxydizing agent and is much used both in labor-
atory work and on a large scale for manufacturing
purposes.

If the superoxyd has the composition Na_2O_2 then
the *oxyd* must be Na_2O.   We get this by fusing
together the hydroxyd with the metal in proper
proportion.   It is a gray substance, and of no spec-
ial application.   It attracts moisture from the air
and becomes hydroxyd.

CHAPTER VII.

THE STORY OF SODA ASH AND LEBLANC.

WHEN in the early years of the past century Napoleon closed all the harbors of Continental Europe to English and American ships, in order to destroy the commerce of England, as he could not destroy its navy, there arose in Continental Europe a scarcity of potash, since the supply had nearly all come from the American colonies. To ease the demand for this article, as well as to spite England, Napoleon offered a prize of 100,000 francs, 20,000 dollars, for the discovery of a substitute for potash. This prize was won and awarded to the French chemist Leblanc, who proposed a process by which common salt can be turned into a body which may be substituted for potash in most technical applications, a process which held its own for 80 years and is only now giving way slowly to better methods. (See Solvay process at end of chap. XI.) All the reactions were known to chemists at the time but one, the replacing of copper oxyd by a cheaper compound. Leblanc found that limestone, or oyster shells, or chalk could replace the copper oxyd, if the action takes place at red heat. To wit:

$$Na^2S + 2CaO.CO^2 + red\ heat = Na^2O.CO^2 +$$
$$CaO.CaS + CO^2.$$
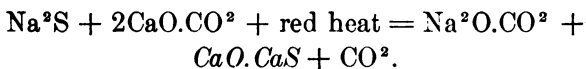
$Na^2O.CO^2$ is easily soluble in water; $CaO.CaS$ (calcium oxysulfid) is insoluble in water, and $Na^2O.CO^2$ is the practical substitute for $K^2O.CO^2$ (potash). The entire run from salt to soda ash is represented in the following symbolic scheme:

(1) $2NaCl$ (salt) $+ 2H^2O.SO^3 +$ heat $= 2HCl + Na^2O.SO^3.H^2SO^3$.

(2) $Na^2O.SO^3.H^2O.SO^3 +$ heat $= Na^2O.SO^3$ (salt cake) $+ SO^3 + H^2O$.

(3) $Na^2O.SO^3 + 4C + 2CaO.CO^2$ (chalk) $+$ yellow heat $= Na^2O.CO^2 + CaO.CaS + CO^2 + 4CO$ (inflammable gas).

(4) $Na^2O.CO^2 + CaO.CaS +$ water $+$ heat $= CaO.CaS$ (residue) $+ Na^2O.CO^2$ (solution).

(5) $Na^2O.CO^2$ (solution) $+$ evaporation $= Na^2O.CO^2$, soda ash.
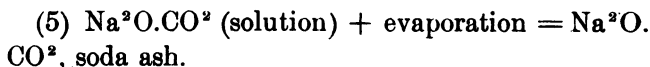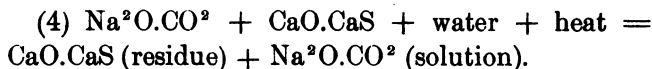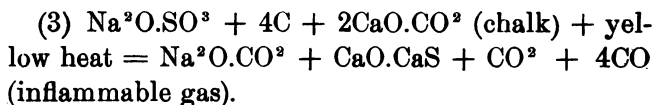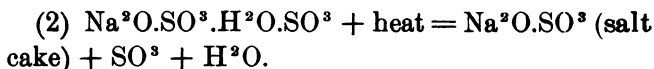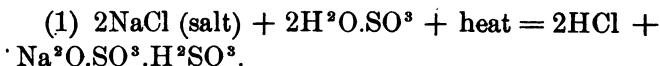
The soda ash produced in this way is not pure: The carbonate predominates, but mixed with it we find $Na^2O.H^2O, Na^2S$ and other impurities. It can be purified; not necessary for most of the applications, such as soap-making. A factory in which soda ash is produced goes by the name of *alkali works*. It is usually divided into several departments, located in separate buildings. (a) Acid works where the sulfuric acid is made. (b) Salt-cake works. (c) Black ash smelter and extractor. (d) White ash works. (e) Bleaching-lime works, where the hydrochloric acid is converted into chlorine and the latter is absorbed by the dry slaked lime.

SODA ASH—SODIUM CARBONATE, SAL SODA, BAKING SODA.

When the liquid resulting from action (4) (see above) is evaporated to dryness and then fired to red heat, the product bears the name *crude white soda ash*. If the same liquid is however only evaporated or boiled down to a certain point and is then allowed to cool slowly, large crystals will form. These are $Na_2O.CO_2 + 10H_2O$ and go by the name *sal soda* (salt of soda). The impurities remain in the mother liquor. If they be exposed on wicker hurdles in an exposed space into which lime gas is conducted from the top of a lime kiln, then they will pass into a fine granular white sandy material whilst water runs away from them. The white powder goes under name of *baking soda, bicarbonate of soda*. The action is thus:

$$Na_2O.CO_2 + 10H_2O + CO_2 \text{ (lime gas)} = Na_2O.CO_2.H_2O.CO_2 + 9H_2O.$$
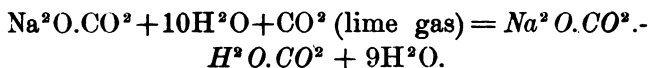
The bicarbonate is slightly soluble in cold water, and at the boiling temperature it breaks up into $Na_2O.CO_2 + CO_2 + H_2O$. If therefore this material be mixed with flour and the resulting dough is put into an oven we will just get that same decomposition, the escaping lime gas causing the raising of the dough. But the bread must taste bitter from the sodium carbonate which remains. In the so-called *baking powders*, the baking soda forms only one ingredient, the other being an acid salt which not only decomposes the carbonate but also removes the bitter taste.

Caustic soda or concentrated lye, of the manufacturers is made by decomposing a 10 per cent. solution of soda ash with one equivalent of slaked lime, the same process we considered under caustic potash. The resulting solution of the sodium hydrate is evaporated, fused and cast into sheet-iron drums, or cans, for smaller quantities, or into one-pound balls, which latter are then dipped into molten rosin. The film of rosin keeps the material from attracting moisture from the air and thus liquefying. The farmers' wives now buy these *lye balls* for their soap-making instead of bothering with the wood ashes. The man who had the idea of the *rosin film* made a fortune from the patent rights.

Certain sea plants growing in the tide levels of France and England, called *kelp* in Wales, and *varec* in France leave an ash which is largely made up of sodium carbonate, the plant's energy transforming the salt into the soda.

CHAPTER VIII.

A CHAPTER ON THEORIES; ON COMBINING WEIGHTS, ATOMIC WEIGHTS AND VALENCES.

THE existence of such bodies as *chlorids*, especially sodium chlorid, containing no oxygen, and yet so much alike to oxygen salts, leads us to thinking. Let us compare hydrogen chlorid, HCl and sulfuric acid, $H^2O.SO^3$. As the symbols stand written, two do not seem at all comparable. But supposing we change the grouping of the elements in the sulfuric acid thus:

$$H^2O.SO^3 — H^2.SO^4,$$
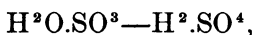
then at first glance we notice the resemblance,

$$H.Cl — H^2.SO^4,$$

and more so still if we place the SO^4 into a bracket,

$$H(Cl) — H^2(SO^4).$$
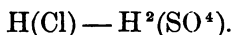
We have no knowledge of an oxyd, SO^4; we only know SO^2, SO^3, S^2O^3, S^2O^4; yet without a great wrench we can imagine that the very moment when the two oxyds, H^2O and SO^3, are brought together, a rearrangement of the elementary particles comes about harmoniously, quite imperceptible to the eye. As soon as we disturb the harmony by trying to remove the hydrogen, then disarrangement, a break-up takes place. But if we accept the reality of

(123)

this unprovable state of things, then the schism in the fundamental chemical phenomena gives way to resolved uniformity. *The acids become then combinations of hydrogen with a non-metallic radical;* the radical can be either one non-metallic element or a group of such elements. In hydrochloric acid, chlorine is the radical, in sulfuric acid the group (SO^4) is the radical. The word *radical* is the adjective of the Latin noun *radix* = root; from the radical, root, arises the stem—the sourness, the acidity. When a metal acts upon an acid, hydrogen escapes. According to the new light we circumscribe this by saying the metal takes the place of the hydrogen:

$$H(Cl) + K = K(Cl) + H$$
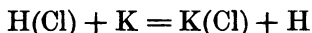
Why does it do so? Because potassium has a stronger affinity for the radical chlorine than hydrogen, and this stronger affinity is made perceptible by the greater quantity of heat which is set free by the union of the two. If Cal. = the unit of heat, then

$$H + Cl = HCl + nCal.$$
$$K + Cl = KCl + n'Cal.$$

$$n' > n.$$

Metals such as lead, copper, silver, gold do not act upon the dilute acids; they are not dissolved by them, because their heat of formation is very small and requires a heat-addition from the external conditions. Thus we can establish a series of the metals in which potassium will occupy the one flank and

gold the other : K., Na., Ca., Mn., Zn., Fe., Sn., Pb.,
Cu., H., Ag., Au.

If we designate K as +, then Na will be negative
in regard to K, but positive in regard to Ca, and
each metal in the same way positive towards its
neighbor on the right, negative towards the one on
the left.   Equally if we place two pieces of sheet
metal upon one another with a moist piece of felt
between, for example, zinc and copper, an electric
tension will show itself between them.   Galvani
observed this 120 years ago, and his name is at-
tached to this electric current even now—galvanic
electricity as against frictional or static electricity.
The series is therefore usually alluded to as the
electro-chemical series of metals.

Of the non-metals, oxygen occupies the extreme
flank, with chlorine next, as sodium stands along-
side of potassium : O., Cl., Br., S., N., C.

Valence.   Glancing at the symbols H(Cl), H^2(SO^4)
we cannot help but being struck by the fact that in
one symbol there is but one hydrogen, whereas there
are two of hydrogen in the other.   We cannot
remove one of these hydrogens without destroying
the harmony, without breaking up the body com-
pletely.   To give expression to this fact we are led
to the term *valence,* a slight difference of meaning
from *equivalence.*   We say the elementary group (Cl)
is *monovalent,* because it finds its satisfaction with
one volume-unit of hydrogen, *monos* = once ; the
compound group (SO^4) is *divalent, dis* = twice, be-
cause it must have two hydrogens to exist.   We

shall find later on elements as well as complex radicals whose valence are 3, 4, 5, 6 designated respectively as *tri-*, *tetra-*, *penta-*, *hexavalent.* I warn you not to be dazzled by these full, sonorous words ; they are but a short cut of speech. You can prove nothing by means of valence, because the expression valence only states a fact, yet is convenient as an expression.

The atomic weights of elements, molecular weights of compounds, volume weights. We find that one volume of chlorine unites with one volume of hydrogen ; in symbols HCl. Chlorine gas is 35.5 times heavier than hydrogen gas hence the symbol stands

$$HCl = 1 + 35.5 = 36.5$$

Also we find that 35.5 grams of chlorine gas combine with 23 grams of sodium and thus produce $35.5 + 23 = 58.5$ grams of NaCl (common salt). Only one compound between Cl and Na has been observed with certainty and this is a very *stable* one. We *assume* that the vapor of sodium, if it could be produced and weighed, would be 23 times heavier than hydrogen, under the same conditions of temperature and pressure. Though the metal volatilizes at red heat yet have all experimental attempts thus far failed, because the sodium vapor attacks all the vessels which are available : platinum, gold, silver, nickel, porcelain ; hence we do know only by *inference* that the volume of the mass unit weighs 23.

Both by composition and decomposition (synthesis and analysis) we know that 35.5 grams of chlorine gas combine with 39 grams of potassium to form

35.5 + 39 grams of KCl. That 39 is the weight of
one volume of potassium vapor we do not know any
better than in the case of sodium, for the same diffi-
culties.   The symbol KCl or NaCl is not a certainty
in other words.   Its strong probability follows from
the following consideration.   By acting upon sul-
furic acid $H^2(SO^4)$ with either of the two metals we
can produce well crystallized salts or vitriols to wit:

$$\left.\begin{matrix} Na \\ H \end{matrix}\right\} (SO^4), \left.\begin{matrix} K \\ H \end{matrix}\right\} (SO^4)$$
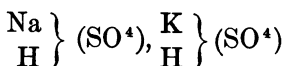
either of which possesses strong acid reaction, and

$$\left.\begin{matrix} Na \\ Na \end{matrix}\right\} (SO^4), \left.\begin{matrix} K \\ K \end{matrix}\right\} (SO^4)$$
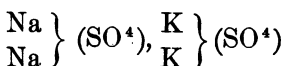
salts which are neutral towards litmus paper.   The
former salts convert into the latter thus:

$2NaH(SO)^4 + $ heat $= NaNa(SO^4) + H^2(SO^4)$ vola-
tilized

$2KH(SO^4) + $ heat $= KK(SO^4) + H^2(SO^4)$ volatil-
ized.
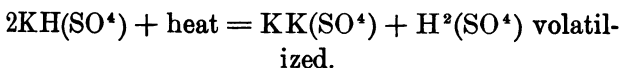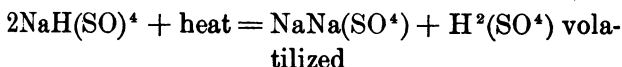
Transposed into numbers this means that we can
combine with one S (32 parts) either 23 or 46 of
sodium, either 39 or 78 of potassium ; but with 23
and 39 only when in each instance there is also one
hydrogen present.   Hence it follows that 23 of
sodium, 39 of potassium, can take the place of—are
equivalent to—one hydrogen in the two acids

$$HCl, \ H^2SO^4.$$
$$KCl, \ K^2SO^4.$$
$$NaCl, \ Na^2SO^4.$$

Potassium, sodium, hydrogen, on these given terms are monovalent metals, or *monads* (a still shorter expression), It is self-evident then that the oxyd of these metals must be Na^2O, K^2O if the oxyd of hydrogen is H^2O. The hydroxyds of the metals sodium and potassium become $Na^2O.H^2O$; $K^2O.-H^2O$. But since we saw in the vitriols one hydrogen being replaced by one Na, or one K, the same must be possible in water, to wit :

$$H^2O + Na = NaHO + H \text{ (escapes).}$$

Hence it follows that the symbol $Na^2O.H^2O = 2$ (NaHO) expresses *two* units or molecules of sodium hydroxyd, that *NaHO* is the true representation of sodium hydroxyd. In the metallic hydroxyd we have, therefore, a combination in which the metal is united to the group (HO). A group which acts as a non-metallic radical of the value (valence) one. This group contains the metal H and the non-metal O, whilst the negative or non-metallic group (SO^4) contains the two non-metals. Perhaps in this hybrid nature of the group (HO) lies part of the reason for the action of the hydroxyd towards litmus and other actions totally opposed to the acids. The relative action, then, of the hydroxyds and acids is this :

$$Na(HO) + H(Cl) = NaCl + H^2O,$$
$$2Na(HO) + H^2(SO^4) = Na^2(SO^4) + 2H^2O.$$
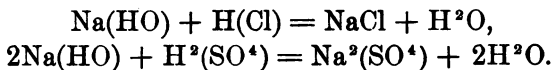
Two attractions exist to account for the powerful action : First the greater attraction of the metal to the non-metallic radical and the tendency of (HO)

to become H^2O by taking another H.   Owing to
the important role of the group (HO) the name
hydroxyl (*ulé* = matter) is given to it.   Hydrogen
= the generator of water, hydroxyl = the matter
from which water is made. ˙ In the light of all these
considerations and speculative deductions, the pre-
vious definitions of base, acid, salt shall be changed
to read as follows:

Base = Combination of metal with one or more
hydroxyl groups.

Acid = Combination of a non-metallic group or
radical with one or more hydrogens.

Salt = Combination of a metal with a non-metal-
lic radical.

The definitions of acid and salt are identical.
The two things are of *one kind*.   *Sulfuric acid is
hydrogen vitriol.*

The term vitriol has been abandoned for the sake
of greater uniformity of chemical expressions.   Its
place is taken by the word sulfate, hence the fol-
lowing:

$H^2(SO^4)$ = *Hydrogen sulfate* = sulfuric acid.

$Na^2(SO^4)$ = Sodium sulfate.

$NaH(SO^4)$ = Sodium, hydrogen sulfate.

$K^2(SO^4)$ = Potassium sulfate.

$KH(SO^4)$ = Potassium, hydrogen sulfate.

$Ca(SO^4)$ = Calcium sulfate.

$Fe(SO^4)$ = Ferro sulfate (iron sulfate).

$Cu(SO^4)$ = Copper sulfate.

$Pb(SO^4)$ = Lead sulfate.

$Zn(SO^4)$ = Zinc sulfate.

9

You should accustom yourself to use the expression: hydrogen sulfate in place of sulfuric acid, though no harm is done by the latter. Logical consequential speech leads to logical thought and work.

Atomic weight of calcium, copper, lead, zinc. By analysis we find that 35.5 grams of chlorine unite with 20 grams of calcium to a stable chlorid. If 20 were the representative of one volume of calcium vapor then the symbol of the chlorid would be CaCl, as NaCl. But we find that we can combine the calcium with the hydrogen sulfate, $H^2(SO^4)$, only in *one way*, not in two ways as with potassium and sodium, namely, so that 40 of calcium correspond to one (SO^4) or one S, that therefore the number 40 must stand for the atomic weight of calcium, that one calcium is equivalent to two hydrogens and therefore the symbol of the chlorid must be written $CaCl^2$.

$$\text{not } 20Ca + 35.5Cl = CaCl,$$
$$\text{but } 40Ca + 2 \times 35.5 = CaCl^2.$$

Copper, zinc, lead, also form only one kind of sulfate, $Cu(SO^4)$, $Zn(SO^4)$, $Pb(SO^4)$, therefore, we say these metals are *divalent* like calcium, their unit weight stands for *two* hydrogens, and in each case 35.5 chlorine combine exactly with one-half as much metal as 32 sulfur, hence their chlorids are $CuCl^2$, $ZnCl^2$, $PbCl^2$. Copper makes an exception in so far as it can unite with chlorine in two ways, to wit: $35.5Cl + 31.5Cu$ and $35.5Cl + 63Cu$. The compound whose ratio of Cl : Cu is 35.5 : 31.5 is the stable compound, permanent at ordinary heat and even

up to red heat. But since in the sulfate 32S correspond to 63Cu, therefore we take the number 63 as the representation of one divalent volume of copper and write

$$63Cu + 2 \times 35.5Cl = CuCl^2, \text{ and}$$
$$2 \times 63Cu + 2 \times 35.5Cl = Cu^2Cl^2.$$
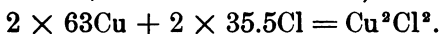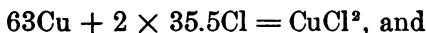
In the first, the stable compound, *cupric* chlorid, $CuCl^2$, the metal is normal, divalent. In the second, the unstable compound, *cuprous* chlorid, Cu^2Cl^2, the metal is abnormal, monovalent. Silver acts like potassium. 107.6Ag combine with one chlorine ; but 2×107.6 combine with one sulfur, 32. Hence *silver is monovalent*, $107.6Ag = $ one H. The chlorid is AgCl, the sulfate is $Ag^2(SO^4)$.

Gold unites with chlorine in two ways. In one compound, which is a white, powdery substance, we find 196Au with 35.5Cl, in the other 65.33Au with 35.5Cl. The first compound is so unstable that it falls to pieces upon the addition of water. In the other compound the chlorine acts upon certain substances as free chlorine. Besides, the specific weight of gold—19.5—is so high that necessarily the weight of its vapor must be very high (though we cannot make this vapor). We take, therefore, 196 to represent the weight of one volume, and write the symbols of the two chlorids :

$$196Au + 35.5Cl = AuCl = \text{aurous chlorid,}$$
$$196Au + 3 \times 35.5Cl = AuCl^3 = \text{auric chlorid.}$$
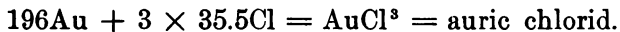
Auric chlorid is a deep yellow substance, easily soluble in water, and fairly stable. In it gold =

Au has the valence 3. In aurous chlorid Au has the valence 1.

Molecular weight. Two or more simple bodies united into a chemical union form a *molecule.* By some it is contended that in the free state even the simplest bodies—the elements—form molecules, that in the free state hydrogen is $(H.H) = 2$, chlorine $(Cl.Cl) = 71$; oxygen $(O.O) = 32$, and $H^2(SO^4) = 98$ of course. When chlorine acts upon hydrogen the action must, according to this view, be represented by :

$$\binom{Cl}{Cl} + \binom{H}{H} = 2HCl.$$
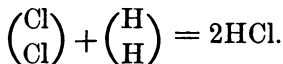
Nothing is changed, in reality, by adopting this view, or by rejecting it. If we speak of molecular weight we shall invariably mean that the molecule is composed of several elements.

Relation between atomic weights and specific heat of the elements. By *heat capacity* the physicists understand the quantity of heat energy expressed in *calories* (heat units), which is necessary to raise the temperature of a mass equal to one gram of a substance by one degree of the centigrade thermometer. The *specific heat* of a body (solid or liquid) means its heat capacity referred to that of water as the unit. The specific heat of gases is referred to that of air or also to that of water as units. The variation of values thus obtained is highly astonishing. In general, the heat capacity of metals is very low, that is, a metal shows the heat very quickly, water very slowly. The numbers representing the specific

heats are therefore always true decimal fractions. *When the atomic weights of the metals are multiplied by their specific heats the product is a constant.* Reason therefore demands that whenever the product is not equal to the constant, there must be something wrong, that we stand before a riddle. The following numbers show this relation, which is also known as the "Law of Dulong and Petit:"

		A. W.	Spec. Heat.	Product.
Silver	Ag	108	× 0.0570	= 6.156
Iron	Fe	56	× 0.1138	= 6.375
Copper	Cu	63	× 0.0952	= 5.99
Zinc	Zn	65	× 0.0955	= 6.207
Calcium	Ca	40	× 0.167	= 6.68
Sodium	Na	23	× 0.2930	= 6.73
Potassium	K	39	× 0.1655	= 6.45
Lead	Pb	207	× 0.0314	= 6.499
Tin	Sn	118	× 0.0562	= 6.631

These numbers do not show exactly the same product for all the metals, but the constant appears to be about *6.5.*

Inversely it would follow that the *specific heat of the atomic volume is the same for all the metals;* the specific heat is an inverse function of the *mass;* the greater the specific gravity, the smaller the specific heat.

REVIEW OF THE ACTION OF CHLORINE ON THE ALKA-LINE HYDROXYDS.

The action of chlorine upon the alkaline hydroxyds is so important, theoretically and practi-

cally, that we must now transcribe the symbols for those reactions according to the notion of valence :

1. $2K(HO) + 2Cl = K(ClO) + H_2O$. The radical (ClO) should be called *chloryl* like hydroxyl, but this name is rarely met with. It cannot be isolated, it has no real existence, it is unbalanced ; Cl^2O is the balanced or saturated molecule.

Cl^2O—*Dichloroxyd* is at ordinary temperature a reddish-yellow gas of penetrating odor. Specific gravity = 2.977. 1 cubic centimeter weighs 0.0039 grams, nearly 4 mgs.; 1 c.c. of chlorine weighs 0.00317; 1 c.c. of oxygen weighs 0.00143. 2 volumes $Cl + 1$ vol. $O = 2 \times 0.00317 + 0.00143 = 0.00777$. If the latter sum be divided by two we get 0.00388 which is equivalent to the experimental weight 0.0039. Hence it follows that $2Cl + 1O = 3$ vols., in combining to Cl^2O *contract one-third*. We found this to be so for SO^2 and for H^2O. We may deduce the general law that *two volumes of one element combining with one volume of another element always produce two volumes of the combination.* Thus is explained why the unit weight of a compound can be greater than the sum of the unit weight of its composing elements.

Cl^2O becomes a blood-red liquid, when the gas is conducted into a tube which stands in a freezing mixture. The liquid is terribly explosive. A scratch with the file on the glass tube may cause an explosion; the Cl^2O just breaking up into $Cl^2 + O$. This is an interesting fact. For in spite of Cl^2O being a compound like water H^2O, yet whilst the

latter is strongly cohering, the former has little coherence, because in Cl^2O we have *two non-metals*, whilst in H^2O we have *metal and non-metal*. The compound Cl^2O is made by acting with chlorine upon the oxyd of mercury, thus: $HgO + 4Cl = HgCl^2 + Cl^2O$ (reddish-yellow gas). In its actions upon metals this body is more energetic even than chlorine itself.

When chlorine acts upon $K(HO)$ or $Na(HO)$ or $Ca(HO)^2$ at *boiling heat* the following actions occur:

$$6K(OH) + 6Cl + \text{boiling heat} = K(ClO^3) + 5KCl + 3H^2O$$

$$6Na(OH) + 6Cl + \text{boiling heat} = Na(ClO^3) + 5NaCl + 3H^2O$$

$$6Ca(OH)^2 + 12Cl + \text{boiling heat} = Ca(ClO^3)^2 + 5CaCl^2 + 6H^2O$$
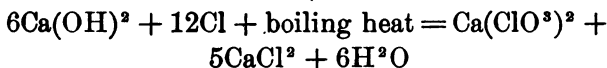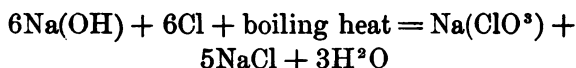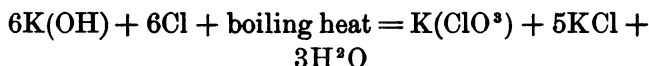
The important products are $K(ClO^3)$, $Na(ClO^3)$, $Ca(ClO^3)^2$. These bodies we will designate *chlorates*. The group (ClO^3) is a monovalent radical but has no real existence; neither do we know the corresponding chloroxyd Cl^2O^5. But we can prepare the *hydrogen chlorate*, $H(ClO^3)$. It forms a thick, syrupy liquid at ordinary temperature, has strong acid taste, no odor. Above 40° C. it begins to give out chlorine and oxygen.

Potassium chlorate, is as above stated, the most important of the chlorates, because with it we can generate chlorine gas easily in immediate contact with the bodies to be acted upon:

$$KClO^3 + \text{water} + 6HCl = KCl + \textit{6 Cl} + 3H^2O.$$
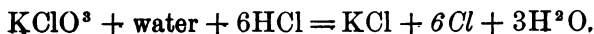
Generation of pure oxygen gas by means of potassium chlorate.

Equation $KClO^3 + \text{heat} = KCl + 3O$
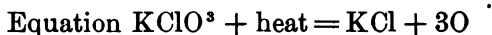
Converted into figures this means: Molecular weight of $KClO^3 = 39 + 35.5 + 3 \times 16 = 122.5$ grams, give 48 grams oxygen gas. One cubic centimeter of oxygen weighs 0.00143 grams, hence 48 grams $= \frac{48}{0.00143}$ c.c. $= 33636$ c.c. $= 33.636$ litres $= 0.033636$ cubic meter.

Problem. Let a gas holder be a sheet-iron cylinder with the dimensions: Diameter $= 13.5$ inches, height $= 27$ inches. How many grams of potassium chlorate will be required to fill this holder with oxygen? 1 inch equals 2.5 centimeters $= 0.025$ m.

BROMINE, IODINE, FLUORINE.

BROMINE.

In the process of salt-making from natural and artificial salt wells, the brine (salt solution) is evaporated. At a certain concentration of the boiling liquid, salt crystals fall out and keep on precipitating up to a given point. The crystals are steadily removed by means of a sieve-ladle. Finally a heavy solution remains from which no crystals of salt fall. This solution is the *mother liquor.* It contains the chlorids of calcium and magnesium, $CaCl^2 + MgCl^2 + x$, x being the combination of the new element *bromine*, from Greek *bromos* = stench, with *magnesium*. If the mother liquor be heated with H^2SO^4 and MnO^2 the liquid becomes dark red-brown and heavy red-brown vapors appear above it. The vapors condense in a water-cooled receiver to a deep red-brown liquid, almost black, and emit a strong, irritating, suffocating odor (indicated in name). Specific gravity = 3.187 at 0° C., 2.97 at 15° C. It boils at 63° C. and 760 mm. It becomes a brown-red, crystalline solid at —24° C. The symbol for bromine is Br. Bromine gas is 80 times heavier than hydrogen. In most of

its chemical actions it is similar to chlorine. It is soluble in water; 1 part of bromine dissolves in 33.3 parts of water at 15° C. The solution is blood-red in color, and gives off bromine vapors. It is soluble in ether, alcohol, chloroform and carbon disulfid. If a water solution, containing little bromine, be shaken with carbon disulfid, the bromine will leave the water and pass into the carbon disulfid.

1 vol. Br. + 1 vol. H + heat = 2 vols. HBr.
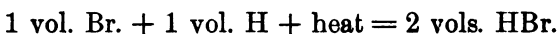
Hence Br is monovalent like chlorine. The resulting HBr, *hydrogen bromid* is a colorless pungent gas like HCl. Liquefies at —73°C. into a colorless liquid, which becomes solid when the liquid HBr is allowed to evaporate in the air. One c.c. weighs 0.003616 gr. HBr is eagerly absorbed by water, and is then named *hydrobromic acid*. The highest concentration is 82 per cent. HBr, corresponding to HBr + H^2O. HBr dissolves metals except Ag, Cu, Hg, Pb, because the resulting bromids AgBr, Cu^2Br^2, Hg^2Br^2, $PbBr^2$, are not soluble. HBr combines with the hydroxyds, as HCl does thus

$$Na(HO) + HBr = NaBr + H^2O,$$
$$Ca(HO)^2 + 2HBr = CaBr^2 + 2H^2O.$$
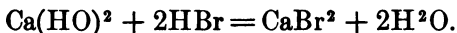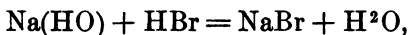
Bromids and oxybromids form when bromine acts upon the alkaline hydroxyds, thus:

$$2Na(HO) + water + 2Br = NaBr + Na(BrO) + H^2O,$$
$$6Na(HO) \text{ (concentrated)} + 6Br = 5NaBr + NaBrO^3 + 3H^2O,$$
$$6K(HO) \text{ (concentrated)} + 6Br = 5KBr + KBrO^3 + 3H^2O,$$
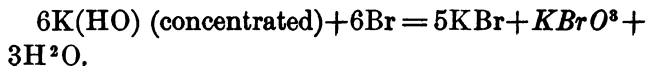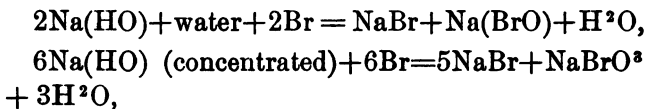
Potassium bromate, KBrO³, is even more insoluble than KClO³. If therefore bromine be added to concentrated solution KOH (1:3) until the liquid retains a permanent yellow color, KBrO⁴ will fall out as a crystalline, colorless powder; KBr remains in solution. KBrO³ can be made pure by dissolving the powder in boiling water, when the salt will crystallize on cooling.

The most important salt is *sodium bromid, NaBr.* It forms a part of *bromo seltzer ;* is much prescribed by physicians against headache. Tons of it are consumed annually.

Bromine itself and bromine water are valuable oxidizing agents in the hands of the chemist. Thus,

$$SO^2 + 2H^2O + 2Br = H^2(SO^4) + 2HBr.$$
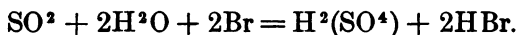
Upon heating the solution, HBr escapes with aqueous vapor and leaves hydrogen sulphate. There are many similar actions, with which we shall meet hereafter.

IODINE.

Before the discovery of bromine a French chemist, Courtois, had found a strange action in the mother liquor of the varec. By this name the peasants of the Channel Coast in northern France designate the extract from the ashes of the sea weeds which are thrown ashore by the storm. These ashes show alkaline reaction like the ashes of land plants, but it was recognized that the *sodium carbonate* is the principal component, not potassium carbonate, as in wood ashes. When the strained lye

from the water extraction is boiled down, potassium sulfate falls out first (being least soluble), then falls $Na^2SO^4 + 2H^2O$, then NaCl, then $Na^2CO^3 + 3H^2O$, finally leaving a mother liquor quite strongly alkaline, but containing still NaCl, together with Na^2CO^3 and small quantities of sulfur-compounds of sodium.   To this mother liquor H^2SO^4 + water (1.7 sp. g.), *pan acid*, is gradually added until the solution is decidedly acid. CO^2 escapes and hydrogen sulfid, while a scum forms, chiefly consisting of sulfur.   After this scum has been dipped out and the solution has become quite clear, it is transferred into a retort (cast iron with a leaden alembic or cap), manganese dioxyd is added and heat applied. Iodine vapors are given off which become a black crystallized sublimate in the receiver, made of earthenware.   It is, however, impure with salts and water.   The water is allowed to drain off, the residue redistilled with quicklime, which absorbs the remaining moisture.   The nitre works of Chili furnish a mother liquor from which large quantities of iodine are manufactured.   So also from the mother liquor of the chemical works at Stassfurt, Germany. In fact iodine or rather an iodid (either NaI or MgI^2) is contained in the sea water, thence it gets into the algae (sea weed); also into the salt beds of the earth ; thence into all salt springs and wells. More in some places than in others.   The sea weed contains up to 0.6 p. c. of iodine, but most of it gets lost in the drying and the burning.   All iodine producers are in a big trust, maintaining high prices. Probably a million pounds are consumed annually.

Properties.   At ordinary temperature a grey-black solid, *always crystals* or crystal fragments; metallic lustre; emits a strong, unpleasant odor.   It is very soft.   Sp. G. 4.958.   Melts at 107° C.; boils at 180° C.   The vapor of iodine is of a beautiful *violet* color.   The name iodine from *iodos* — similar to violets, was given for this color, which is so very characteristic and even unique.   Water does not dissolve iodine freely.   One gram I dissolves at 10–12° C. in 5524 grams of water.   This solution is known as iodine water.   It *bleaches* the same as chlorine water.   Much more soluble in alcohol. This solution is known as *tincture of iodine*, much used by physicians, to relieve swellings of the skin. Makes a dark-brown stain on the skin, on wool or silk.   Iodine dissolves readily in a water solution of potassium iodid, KI, giving a yellow, brown or blood-red liquid.   Soluble in ether, in carbon disulfid.   If a trace of iodine be contained in much water, or salt solutions, a few drops of carbon disulfid, shaken with the water, will absorb all the iodine and assume a rose color or purple color.   The vapor of iodine is 127 times as heavy as an equal volume of hydrogen at the same temperature. Hence 127 is the atomic weight; the symbol is I.

Starch and iodine.   If starch be boiled to thin paste, and the paste filtered, making a clear solution, then this colorless solution will become intensely *blue* if a small quantity of iodine solution be added.   Starch + iodine equals *blue body*.   Thus we can recognize starch from other parts of a plant

or seed by means of iodine, and detect iodine in solution with other bodies.

Chemical properties. Iodine combines with the metals directly forming *iodids.* $K + I = KI$ (with explosive energy), $Na + I = NaI$, the two elements melt together without explosive display. $Hg + 2I + heat = HgI^2$ (producing light) a scarlet-red body. $Hg + I = HgI$, a green-yellow body. These iodids are decomposed by bromine;

$$KI + Br = KBr + I.$$
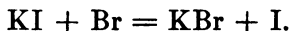
Then in its turn $KBr + Cl$ give $KCl + Br$.

Chlorine, bromine, iodine form a series whose chemical affinity is *inversely* as their atomic weights which are 35.5, 80, 127. The greater the mass, the more sluggish the activity.

Iodine does not readily combine with hydrogen, as chlorine does. It requires a high temperature. (6030 calories.)

Hydroiodic acid, HI + water is best prepared by working along the equation

$$2I + H^2S + water = 2HI + water + S.$$
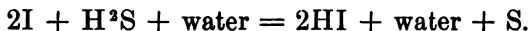
We keep the finely powdered iodine stirred up in water whilst the gas H^2S is passed into the water; the color of the solution disappears. HI is then dissolved in the water, the sulfur is to be removed by filtration. The liquid is strongly acid, smells pungent like HCl and acts upon metals and hydroxyds in a general way the same as HCl. A solution of $Ag^2SO^4 + HI +$ water gives a *yellow precipitate of AgI*, while HCl produces a *white precipitate of AgCl.*

One does not often have occasion to prepare and use HI.

Oxyiodids, iodates, hydrogen iodate, HIO³. By the action of iodine upon KHO we obtain KI and $K(IO^3)$. $6KHO + 6I = 5KI + K(IO^3) + 3H^2O$. Potassium iodate is slightly soluble in water. If $K(ClO^3)$ be dissolved in water, to the liquid finely powdered iodine added and the solution boiled, then the iodine will displace the chlorine.

$$5K(ClO^3) + 6I + 3H^2O + heat = 5K(IO^3) + 5HCl + HIO^3.$$
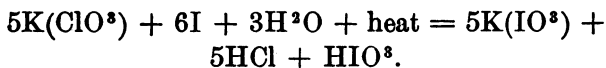
From an iodid as KI—chlorine displaces iodine; but from a chlorate iodine displaces chlorine, we say: Iodine has a stronger affinity for oxygen than chlorine. We make use of this property in quantitative analysis.

H(IO³), Hydrogen iodate, iodic acid is formed by acting with chlorine gas upon water in which finely ground iodine is suspended—

$$3H^2O + I + 5Cl = H(IO^3) + 5HCl.$$
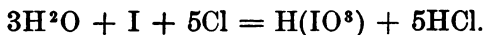
If a dilute solution of $NaIO^3$ be heated and chlorine be passed through until no further precipitation of salt be noticed, then the precipitate is $Na^2(IO^6)H^2$ or $Na^2O.H^2O(IO^4)$ *sodium hydrogen periodate*, and from this can be made the silver salt $Ag(IO^4)$, *silver periodate.*

General remarks. The most important compound of iodine is KI, potassium iodid, which forms white or colorless cubic crystals, like KBr, KCl; the three salts are *isomorphous,* have equal form and can re-

place each other in any crystal. We can have a crystal, any particle of which contains K, Cl, Br, I, even the very smallest. This leads us to the conclusion that Cl or Br do not in reality stand for one smallest unit, but that they represent a vast number each of smallest units; roughly, the circle represents the *active unit*, but the dots mean smallest particles so that one active unit may contain any number of isomorphous particles as Cl, Br, I. The two spheres, Fig. 42, mean the molecule K(Cl, Br, I).

FIG. 42.
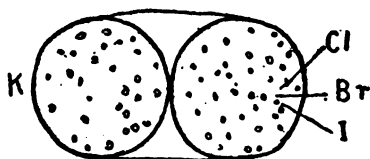
The sphere representing potassium contains also a multitude of smallest particles, which in their turn may be a mixture of any number of isomorphous metals, such as Na, Ag. That is, the smallest fragment of a microscopic cube might contain (K, Na, Co, Rb, Tl), (Cl, Br, I). Minute quantities of iodine are found in the blood of man and animals as well as in plants, more particularly in the bones of the animal. We find iodine in the mineral *iodyrite*, AgI, among silver ores in yellow hexagonal crystals.

FLUORINE.

The mineral *fluorite, fluorspar* from German *fluss-spath*, occurs widely as *gangue* (German *gang* = vein)

or vein-matter with silver-lead ores, sometimes filling considerable fissure veins all by itself. The German miners call all minerals which are transparent or translucent and possess strong cleavage, *spath*, thus calcite is *kalkspath*, iron carbonate is *eisenspath*, orthoclase is *feldspath*, and our present mineral was named flussspath because the smelters noticed that it melts not only by itself, but causes other gangue minerals to become fluid, in other words, to act as a *flux* in smelting. *Fluss* = flux, whilst *fluere* is Latin for *to flow*.

Fluorite is characterized by its isometric crystals, cubes, octahedrons, tetrahexahedrons, hexoctahedrons, and its strong cleavage parallel to the faces of the octohedron. It scratches calcite, is therefore harder. Mostly colored green, purple, pink, blue, black, yellow, yet these colors are accidental, do not belong to the substance of the mineral itself, which is colorless or white. Shows no taste, therefore insoluble in water.

Fluorite melts just at the temperature glass melts; experiment to be made in a small platinum spoon or crucible; no gas will be given out. If, however, we put a piece of the spar upon charcoal and direct a strong oxydyzing flame upon it, the spar will melt at first, but after some time will solidify. Why? Because the conditions are different from those in the crucible. The flame itself is not a mere source of heat, but a mixture of gases at high temperature. Among the gases are aqueous vapor and oxygen (from the air). We know both to be powerful

10

agents when assisted by heat.   Indeed, by bringing
the nose near the charcoal, a pungent odor becomes
noticeable ; the spar decomposes under the influence
of aqueous vapor and heat and oxygen.   The residue
assumes more and more the appearance of lime,
glowing incandescence.   By acting upon the finely-
powdered spar with H_2SO_4, in a test-tube, there
appears no action at ordinary temperature.   Upon
applying heat, gas bubbles arise, slowly at first,
finally in large number, so that the liquid froths.
A gas evidently escapes.   To the nose the gas is
pungent, acrid, recalling HCl, but more repelling.
Litmus turns red at once in the gas.

Investigation of the gas.   Hypothesis : Having an
odor like HCl, we may infer that the gas is a com-
pound H^nX^m or perhaps simply HX ; and proceed-
ing a little further with the assumption that X is a
new element, let X at once be represented by the
letter F (first of fluor spar) ; hence the gas may be
H^nF^m or perhaps HF.   At the outset in the in-
vestigation, we find ourselves confronted with a
serious difficulty.   Namely we find the test-tube,
which was used in the first experiment, strongly *cor-
roded*, after it is washed out with water : The gas
evidently decomposes glass.   This unwelcome fact
it is true puts a sure stamp of originality upon the
new element, quite unlike any other thus far met
with, but at the same time excludes the use of glass
tubing and all other glassware.   On porcelain it
acts as on glass ; on iron and zinc it acts strongly,
also on copper and silver.   Not so on lead, gold and

platinum, nor on wax, paraffine or rubber. The
latter materials do not stand heat. We are thrown
then upon the three metals, of which lead is the
cheapest. The gas acts somewhat upon the lead
surface, but the product of the action being nearly
insoluble, the metal answers well enough for all
ordinary purposes. We construct a distilling ap-
paratus of which Fig. 43 gives a sectional represen-

FIG. 43
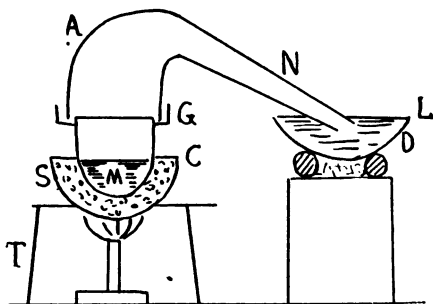
tation. C is a cup of sheet lead with a ring-shaped
groove G at the rim. The cup sits in an iron cup
forming a sand bath, this resting on the tripod T.
Into the groove G fits the alembic or helmet A,
with the tube neck N. After filling the mixture of
fluorite powder and H_2SO_4 (so much acid that a
thin mush forms) at M into the cup C, the alembic
A is set into the groove G, and the latter filled with
plaster of paris and water. The plaster *sets* and
forms a gas-tight joint. The platinum dish D is
partly filled with pure water and so placed under
N that the water level L just covers the mouth of

N. *D* may be set into another dish and surrounded with snow and ice or salt. When the lamp is put under the sand bath, the air is first driven out, then the gas appears and dissolves in the cold water. **If** we substitute a cylindrical bottle of lead or platinum for the dish, the gas itself will condense into a liquid; specific gravity at 12° C. 0.988, nearly equal to water. This liquid boils at 19.5° C. It fumes in the air; the gas combining with the moisture of the air gives the visible fume. Fumes cause violent coughing, and may produce death if taken into the lungs. A drop of the liquid will produce on the skin a white spot, a blister forms, bursts and a painful, slowly healing ulcer forms. Be very careful with this concentrated liquid; but even the dilute water solution has given one much discomfort, when some of it got under the finger nails. The perfectly dry gas does not attack glass; the least moisture causes an immediate attack ; the glass becomes *opaque*, we say the fluorspar gas, or liquid, *etches* glass; German *aetzen*, French *mordre* = to bite. To etch means to bite out something.

Composition of the gas. When the gas acts upon Na, K, Zn, Fe, two products arise: Hydrogen $+$ Me^nF^m (metallic fluorid). When it acts upon hydroxyd: $H^2O + Me^nF^m$ result.

$$KHO + H^nF^m = K^nF^m + H^2O.$$
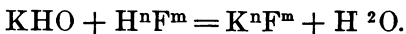
That the gas is a hydrogen compound of the radical F there can be no doubt. But there is a difference about the valence of F. Because there is, as with

the molecule H^2SO^4 (see above) the existence of two salts to wit $NaHF^x$ and NaF^x. In the latter 23 Na (sodium) are combined with 19 fluorine (F), but in the former 23 Na are combined with one H and 38 F. If we admit the proof power of this acid salt (as with the sulfate) then fluorine (F) is divalent, the sodium fluorid is Na^2F, the atomic weight of $F = 38$. There are, on the other hand, quite weighty reasons why we should assume F to be monovalent. Chiefly the closeness between its action and that of chlorine is convincing to the large majority of chemists to declare fluorine a monad and its atomic weight $= 19$.

Sodium fluorid is thus made NaF. The acid salt is $NaH(F^2)$. The solution of HF in water is hydrofluoric acid. The acid is in all actions closely like HCl, in some instances however fluorids are unlike chlorids. When a water solution of silver sulfate is added to $HF +$ water, no precipitate falls, the AgF being easily soluble in water, whilst AgCl is insoluble in water. On the other hand, calcium chlorid $CaCl^2$ is very soluble in water, calcium fluorid CaF^2 is insoluble in water.

The etching process. We need in the laboratory graduated glass vessels, tubes and flasks ; or we want to mark and number the vessels. Hydrogen fluorid, or the acid salt $NaHF^2$ is invaluable for this purpose ; they can be bought ready for use, being sold either in caoutchouc or *ceresine* bottles (ceresine is mineral wax). First cover the glass with a thin film of paraffine or of wax. Melt these materials,

warm the glass and apply the liquid material with a
brush.   After cooling draw the mark or number upon
the wax or paraffine film ; then scratch away the film
(with a steel point) all the lines or dots which are to
appear in the etching.   After this two ways are
open : (1) to expose the engraved spot to the slow
vapors of HF (this gives the best result); or, (2) to
apply the liquid HF by means of a camel's hair
brush repeatedly, according to the desired depth of
the etching.   There is a so-called *glass ink* on the
market which appears as a milky white liquid.   It
is a solution of the acid salt $NaHF^2$ mixed with
plaster of paris.

   The nature of fluorine.   When HF is made to act
upon metallic peroxyds as MnO^2, water is produced,
MnF^2 and a mixture of oxygen with fluorine.
Many statements by experimenters are on record
contradicting each other.   The work is exceedingly
difficult and expensive.   No pure fluorine has as
yet been obtained by the above method.   This
much seems certain, that fluorine possesses a color
similar to that of chlorine, *i. e.* yellowish-green, that
its odor is similar to that of chlorine, that it attacks
all substances except fluorspar, especially platinum
and glass, and bleaches indigo.   This state of affairs
explains why we are uncertain about the valence
and the atomic weight.

   The metal contained in fluorspar.   After the mix-
ture of spar powder with H^2SO^4 has been heated
until HF no longer escapes, but the thick white
fumes of H^2SO^4, that means when complete decom-

position has taken place, we find the residue to be a semi-solid which is soluble in a large quantity of water. From the solution precipitate characteristic monoclinic crystals of calcium vitriol = calcium sulfate or gypsum. There may be minute quantities of other metals, which do not now concern us. Calcium is therefore the metal of fluorite, it is *calcium fluorid, CaF^2.*

CHAPTER X.

LECTURE ON NITER OR SALTPETER.

SALTPETER or niter is the name at present given to a peculiar salt of immense technical or industrial importance. The word saltpeter is the corruption of Latin = *sal petrae* = salt of the rock; niter is derived from Hebrew-Egyptian = *neter* thence Greek = *natron-nitron*, thence Latin *nitrum*, the meaning of which has been explained above as original for natrium = sodium. At the present time the name applies to something very different from either rock salt or soda. It applies to two salts, *one* forming always prismatic crystals of the orthorhombic system, and *the other* appearing in grains, roughly resembling common salt. On closer examination the granular crystals are seen to possess rhomboid faces not rectangular as in the cube. Geometrically a cube and a rhombohedron are not different except as to the position of the faces in regard to a system of arbitrary axes. It is quite possible that a crystallographic rhombohedron has rectangular faces, and a crystallographic cube has facial angles slightly deviating from 90°. The action of a crystal towards the polarized light alone determines the system of crystallization. The angle of the pole edges is 106° 30′ very near the angle of the cleavage rhom-

(152)

bohedron of calcite, which is 105° 30′. At all
events the obliquity of the angle is large enough to
exclude the idea of the cube.

The prismatic niter is known as *potash niter*, the
granular rhombohedral variety is known as *Chili
niter or soda niter*.   Both varieties are easily soluble
in water, show a *cooling* taste; nevertheless, there
is a marked difference in the solubility of the two
forms of niter.   100 grams of water dissolve

	Soda Niter.			Potash Niter.
at— 6° C.	68.8	at	0° C.	13.3
+ 10° C.	84.3		+18° C.	29.0
+ 20° C.	89.5		+45° C.	74.6
+100° C.	168.2		+97° C.	236.0

Between 0° and 100° C. the ratio of solubility is
for soda niter $\frac{168.8}{79} = \frac{2}{1}$; for potash niter $\frac{236.0}{13.3} = \frac{18}{1}$.
Both niters melt easily.   Potash niter, when held
in the flame, gives a purple color, soda niter a
yellow color to it.   About the localities and condi-
tions where and under which the niters are found,
we will speak at the end of this investigation, as you
will be better able to understand several of the
intricate questions which arise in connection with
these bodies.

Investigation of the soda niter.   Let first a crystal
fragment be heated in a closed tube.   When the
heat rises to redness, we notice gas bubbles.   On
trying the gas we find it to act like oxygen, being
without odor, and being able to fan a dark red
glowing taper into bright incandescence.   Now let

us drop a small piece of feathered tin into the molten
niter. Notice the intense action, emission of light
and conversion of the tin into white oxyd. Repeat
these actions with sulfur, with antimony, with char-
coal ; in all these cases there is displayed the phe-
nomenon of burning, of combustion. Similar action
is displayed by melting potassium chlorate. We
may then rightly infer that niter is a salt similar to
$K(ClO^3)$, or $Na(ClO^3)$, but that the salts are not
identical follows from several reasons: (1) unlike
form of crystals, (2) great difference in solubility,
(3) that the chlorates part with their oxygen easily
at low temperature, whilst niter only parts with it
at red heat, (4) that a brown gas arises from the
niter when it burns up a piece of metal, of sulfur or
wood, (5) that this brown gas is suffocating. The
unavoidable conclusion points to the existence in
niter besides sodium and oxygen, of another un-
known element. Let this element be designated by
N the first letter of niter, and let it be pronounced
nitrogen = generator of niter ; then soda niter will
most probably be $Na^n N^m O^p$, and of potash niter,
$K^n N^m O^p$. What is the nature of N? What is the
ratio of its combination, what are the numerical
values of n, m, p?

(1) *What is the nature of N— of nitrogen ?* Let us
return first to that experiment in which the niter
was heated by itself, yielding oxygen. On acting
upon it with water we will get a solution which
shows strong alkaline reaction ; the niter itself has
a neutral reaction—neither acid nor alkaline. This

may mean that Na^2O has formed, and likewise that a compound has formed with less oxygen than the original niter, *i. e.*, $Na^nN^mO^{p-q}$. Incidentally we noticed a strong corrosion of the glass tube at the places where the niter had been longest exposed to the flame, which suggests Na^2O, because we know from handling $NaOH$ and Na^2CO^3 in the glass tubes that these bodies attack the glass at high heat. In the water solution would either be $Na(HO) + Na^nN^mO^{p-q}$ or only one of the two. Addition of dilute $H^2(SO^4)$ will neutralize $Na(HO)$.

$2NaHO + H^2(SO^4) = Na^2(SO^4) + H^2O = $ neutral ; a further addition of $H^2(SO^4)$ will cause the evolution of a gas of peculiar odor, rather aromatic. The gas *may* be $H^2N^mO^{p-q}$ or not ; at any rate it is a peculiar body. Now let us act with concentrated $H^2(SO^4)$ upon the original niter. At ordinary temperature there is but little if any action, except that the niter seems to dissolve, at least partly, and but a faint odor is noticed. As heat is applied, effervescence ensues. A sour, pungent gas appears, which condenses in a sufficiently cold receiver into a liquid, or else is energetically absorbed in water. In the residue we have sodium hydrogen sulfate + hydrogen sulfate. We pour it into a porcelain dish, and may convert it into salt cake by means of heat ; prove it to be Na^2SO^4 by means of its easy solubility in water and its resistance to crystallization. Only low temperature will induce crystals. The liquid distillate we will name *spirits of niter*. We study its action upon the metals, upon paper, wood,

the skin, wool, in fact upon all bodies known to us and handy to procure.   For remember always that chemistry means try anything upon everthing else. All the actions will be remarkable.

Lead (Pb) + sp. niter + heat=white salt + brown fumes.

Copper (Cu) + sp. niter=blue salt + brown fumes.

Silver (Ag)+sp. niter=white salt+brown fumes.

Filter paper + sp. niter + heat=solution+brown fumes.

Gold (Au) + sp. niter + heat = no action.

Platinum (Pt) + sp. niter + heat = no action.

Tin (Sn) + sp. niter=white oxyd + brown fumes.

Hydrochloric acid (HCl) + sp. niter + heat = brown liquid + brown fumes.

HCl + sp. niter+gold + warm = yellow solution, $AuCl^3$ + brown fumes.

HCl + sp. niter + platinum = yellow-brown solution + brown fumes.

The spirits of niter proves itself thus one of the most powerful agents.   The Arab chemist Geber was the first to mention this body.   The Latin translation of his works speaks of it as *aqua fortis* (the strong water) or *aqua dissolutiva* (the dissolving water) because it dissolved both silver and lead. But the combination of the spirits of salt (HCl) with the spirits of niter went, and still goes, by the name *aqua regia* (the kingly water), because it dissolves gold, the very king of the metals.

On the other hand, if we dilute first the spirits of niter with water, very considerably, then we get *hydrogen* when acting upon either iron or zinc, but not with lead, copper or any other metal; with all of these it is either brown fumes or nothing. Remember the similarity with the actions of oil of vitriol or of the concentrated sulfuric acid. Concentrated acid on the metals gave vitriols and SO^2; diluted acid on iron or zinc gave vitriols and H. Just as SO^2 was demonstrated as an oxyd with less oxygen than the sulfur oxyd which constitutes the sulfuric acid, so it follows logically that in the action of the strong spirits of niter, the brown fumes must

FIG. 44.
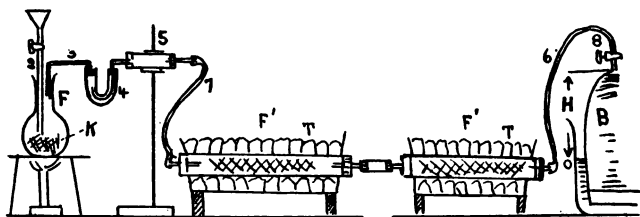
constitute a lower oxyd of the nitrogen, the element whose properties we are after. But if thus the metals can take away oxygen from the nitrogen, we argue, at a temperature below even the boiling-point of water, will it not seem probable that at a still higher heat more will be taken, or perhaps even all?

We set up an apparatus as shown in Fig. 44. *F* is a small flask with twice perforated stopper.

Through the latter pass the stem of a funnel *2* and the delivery tube *3*. In *F* we place finely divided copper, *K* (gauze, granules, chips). The funnels hold the diluted spirits of niter. *3* connects with U-tube *4*. The latter is partly filled with concentrated H_2SO_4 forming a trap to dry and control the escaping gas. *5* is a tube filled with quick-lime (CaO) between two cotton plugs. In the charcoal furnaces *F'*, *F'*, lie the hard glass tubes *T*, *T'*, each charged with rolls of copper wire-gauze. By means of rubber tube *6*, *T'* connects with the bell jar *B*, which is filled with boiled water (in order to expel any absorbed air). Before connecting *F* with tube *7* we heat up the furnaces and pass hydrogen through *T*, *T'*, in order to have perfect metallic surface on the copper. The tube *5* will act as dryer and will also retain any gas of an acid nature. While the action of hydrogen was going on in *T*, *T'*, we have utilized time by starting the action in *F* so that all the air is driven out by the gas. We regulate the flow of liquid from the funnel, so that, if possible, the sulfuric acid trap in *4* will indicate the passing of a slow current of gas. The slower and steadier (not in gulps) the current, the better will be the chances of a perfect deoxydizing action. Before connecting *T* with tube *5* by a rubber tube *7* we remove most of the charcoal from *F*, *F'*, let the tubes *T*, *T'* come down below red heat, for the unknown niter gas, being an oxyd might produce with the hydrogen an explosive mixture. When we connect *7* with *T'* we wait a sufficient time to let the hydro-

gen be displaced by the niter gas, then we replace
the charcoal, get a good heat, cherry red, being
always careful to protect the rubber stoppers in T
and T' by guarding shields and dropping water,
and again after some minutes' wait, we connect the
rubber tube 6 with the bell jar B. In the position
as shown in the figure there will be suction through
the chain of apparatus as soon as the stopper 8 is
opened, owing to the difference of level, h, between
the water inside and outside the bell. Therefore all
stoppers and connections must have been made air-
tight, otherwise air will be sucked into the appara-
tus: The *true nature* of nitrogen will be masked. We
maintain the action until B is filled with gas, or
until several holders shall have been filled.

Properties of nitrogen. After having been pro-
duced, as just stated, the gas possesses the characters
of an element. With present means, it cannot be
further split. A gas devoid of color, odor, taste.
Specific gravity 14 ($H = 1$); 0.9674 ($Air = 1$).
This specific gravity is so nearly the same as that
of the *azote*, the nonrespirable part of the air, this
being 0.9713, that we are justified in declaring azote
$=$ nitrogen, because the nitrogen also is *nonrespir-
able*, it causing death by suffocation. The gas is but
very slightly soluble in water, it is not absorbed by
the alkalies. It is very indifferent towards all
agents, and yet it is evident that under certain con-
ditions it may be made to unite with oxygen in
several ratios, and also with hydrogen giving rise to
a most interesting body. Nitrogen we shall find in

all animal and plant bodies, constituting the essential constituent of *protoplasm*, the body which is at present taken to be the basis, the substratum of all life. It is important to note that nitrogen has no property by which we can at once identify it, except the specific gravity ; all other properties are mere negations of the properties possessed by other gases.

Properties of the spirits of niter and its quantitative composition. Acting with the spirits of niter upon a metallic oxyd (MeO) we get water + niter. The most suitable metallic oxyd for our present purpose is lead oxyd PbO which has the pale yellow color ; the red oxyd is not equally suitable. Acting upon Na(OH) or K(OH) we restore the original niter, either soda niter, or potash niter and water. There is only one salt formed, no acid salt having been obtainable. Hence the radical contained in the spirits is there combined with *one* H, the radical is a monad, and will, therefore, be represented by the symbol

$$H(N^mO^p)$$

Hence, also, if we act with the spirits upon lead oxyd, the reaction must be

$$PbO + 2H(N^mO^p) = Pb(N^mO^p)^2 + H^2O.$$
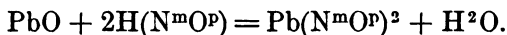
Like the soda and potash niter, the lead niter contains no water, except a trifle with the mother liquor. The white or colorless crystals of this lead niter are rhombohedral, hence isomorphous with the soda niter. It is best, because most rapid, to

use the spirits diluted, because the lead niter is not soluble in the concentrated spirits. When all of the lead oxyd is thus dissolved, or when the liquid will not further dissolve the oxyd, filter and evaporate the filtrate to complete dryness. The residue is then pure lead niter. Heated in a crucible or glass tube, the lead niter breaks up into brown gas and yellow lead oxyd. The brown gas is very acrid and suffocating, yet it will act upon a glowing taper like oxygen. In fact we can readily prove the brown fumes to have an admixture of oxygen; therefore

$$Pb(N^mO^p)^2 + heat = PbO + brown \ gas + O.$$
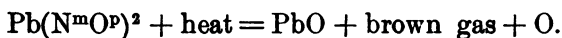
This action opens the way for a quantitative determination of the ratio existing between Pb, N and

FIG. 45.
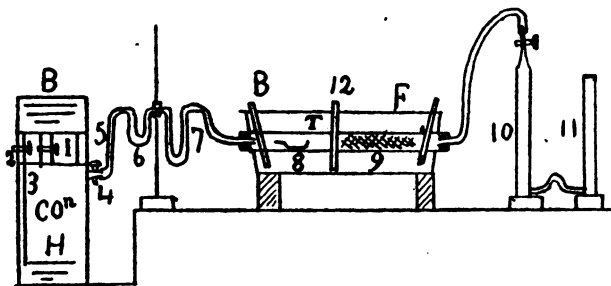
O, if we arrange the conditions of the experiments in such a way that the volume of nitrogen can be accurately measured, which results from the decomposition of say one gram of the lead niter.

Let T, Fig. 45, be an ample hard glass tube fitted

11

with stoppers. *8* is a porcelain boat containing 0.5 gram of lead niter. *9* is a clean roll of copper gauze. *7* is a U-tube filled with pieces of pumice and H_2SO_4 (to retain moisture). *6* is a smaller U-tube with enough H_2SO_4 to form a trap. *H* is the holder filled with lime gas and the water in *B* furnishes the pressure to drive out the gas from *H*. *10* is a gas burette and *11* the cylinder to regulate the pressure. Both cylinders are filled with solution of sodium hydrate. All stoppers and connections being tight, we first displace all air from the apparatus, because four-fifths of it are nitrogen; then heat the copper gauze to redness, while we protect the boat from the heat by the shield *12*. When the gauze is glowing we move shield *12* to the left, from time to time, so that the decomposition of the lead niter shall be slow and gradual; but at length the entire tube is at redness up to the shield. As the niter decomposes the oxygen goes to the copper and the nitrogen passes into the burette, pushing before it the lime gas. As soon as the contents of the boat are pure dark yellow or red, we open the stop cock *4* and drive all niter gas into the burette. Then, closing the latter's stopcock, we shake the gas with the liquid, thus absorbing all the lime gas into the Na(OH) solution, and then read the volume of gas. Let V′ cubic centimeters be the volume of the gas, measured under the pressure of the atmosphere at 20° C, the pressure of the atmosphere, measured by the mercury column of the barometer, be B millimeters. As the gas is satur-

ated with aqueous vapor, being over water, *i. e.*, a dilute solution of Na(HO), the tension T of the aqueous vapor increases the pressure B and must therefore be subtracted, because we wish to get at the volume of the *dry gas*. The expansion of the air for one degree C. is 0.00367 of its volume, hence the volume V° of dry gas at 0° C. and sea level barometer, 760 mm., will be

$$V° = \frac{V'.(B - T)}{(1 + 0.00367t) \times 760} = 33.67 \text{ c.c.}$$

(The tables calculated by Prof. Leo Liebermann are most convenient in such calculations.) If the weight of one c.c. of dry nitrogen at 0° C. and 760 mm. be 0.001256 gram, then

$$V° \times 0.001256 = G,$$

will be the weight of the nitrogen contained in 0.5 gram of lead niter, $Pb(N^mO^p)^2$. G equals 0.0423 gram and the weight of lead oxyd, PbO, is 0.337 gram (found by weighing boat after operation). Then we will have

PbO = 0.3370
N   = 0.0423 ⎱ = 0.163 gram = wt. of the N.
O   = 0.1207 ⎰   oxyd.
      ‾‾‾‾‾‾
      0.5000

The weight of oxygen if found by difference. The volume weights of oxygen and nitrogen (found by direct weighing) are 16 and 14. Hence we will obtain the atomic ratio of the two elements by dividing gram weights of N and O by 14 and 16 respectively.

$$\frac{0.0423}{14} = 0.00302 \; ; \; \frac{0.1207}{16} = 0.00754$$

$$\frac{302}{754} = \frac{2}{5}, \text{ hence } N^2O^5$$

We have directly proved that lead niter is a combination of the oxyd PbO with the oxyd N^2O^5. Above we showed the probability of the radical N^mO^p being a monad. In the lead niter there are then two molecules of the nitric radical.

$PbO.N^2O^5$ becomes $Pb(N^2O^6)$ or $Pb(NO^3)^2$.

For the sake of uniformity we will designate hereafter the niters by the word *nitrate*, thus:

Hydrogen nitrate $= H(NO^3) =$ nitric acid $=$ aqua fortis.

Sodium nitrate $= Na(NO^3) =$ soda niter $=$ Chili niter.

Potassium nitrate $= K(NO^3) =$ potash niter $=$ common niter.

Calcium nitrate $= Ca(NO^3)^2$.

Silver nitrate $= Ag(NO^3)$.

Lead nitrate $= Pb(NO^3)^2$.

Copper nitrate $= Cu(NO^3)^2$.

Ferric nitrate $= Fe(NO^3)^3$.

All normal nitrates are *soluble* in water, whilst some sulfates, some chlorids, bromids, iodids, fluorids are *insoluble* in water.

Sol. $Ag(NO^3) +$ sol. $NaCl =$ insol. $AgCl +$ sol. $Na(NO^3)$.

Sol. $Pb(NO^3)^2$ + sol. $Na^2(SO^4)$ = insol. $Pb(SO^4)$ + sol. $2Na(NO^3)$.
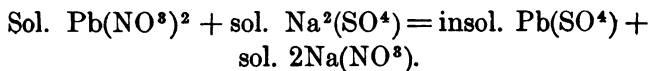
These two reactions serve us as tests for *soluble* chlorids and sulfates respectively.

Of all bodies we have investigated, the nitrates appear to me the most wonderful. The very same elements in which we breathe and lead a more or less harmless life, the existence of which elements we are not even ordinarily aware of, become violently active in the form of nitrates. The chlorates, though acting similarly, are not so astonishing, because in them we find chlorine, a violently offensive body by itself. A rather rough simile may bring nearer to your grip of imagination this action of the nitrates. Let the atoms be imagined as spiral springs (watch spirals). In the atmosphere the nitrogen molecules lie alongside of the oxygen molecules as uncoiled springs, inert, inoffensive things. A powerful shock strikes the inert, uncoiled bodies, say the electric spark of a thunder storm ; the shock causes the springs to coil up, and the affinity of a strong basic oxyd, as K^2O, Na^2O, lies handy as a binding rope of the springs, as shown in Fig. 46 ; the nitrate molecule is achieved ; the potential energy of the coils is restrained by the thin band of affinity. Now let the nitrate molecules be brought into intimate contact with other molecules which possess a stronger affinity for oxygen than the nitrogen, for instance, carbon molecules, at a red heat. We may even carry the picture further and say the thermic energy expands the springs,

straining them against the restraining bond until
at red heat this bond snaps, giving way to carbon
—oxygen attraction. With the breaking of the

FIG. 46.
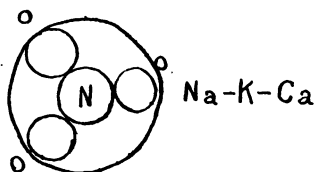
bond, the oxygen springs uncoil and display an
extraordinary energy, such as we are forced to ad-
mire in gunpowder.

COMPOSITION OF GUNPOWDER OR BLACK POWDER.

We saw in a small experiment how the mixture
of niter and charcoal powder flew out of the glass
tube with a flash. The products of that action were
$Na^2(CO^3)$, sodium carbonate, N, nitrogen and
CO^2. The two latter gases, through their expan-
sion, impart to the explosion its propelling or its
tearing, splitting effect. The more gas, the greater
the effect from a given mixture. But in forming
Na^2CO^3 much gas passes into the solid state and
lessens the effect of the powder. It was soon found
that a greater effect could be obtained by mixing
with niter and charcoal a certain quantity of sulfur.
This was all arrived at by those patient experi-
menters without knowing even that the production
of gas was the chief object. They mixed sulfur

with the powder on general principles that it would
be a good thing, because sulfur was a very peculiar
and mysterious body. · We modern chemists, who
experiment less and think more, know why the sul-
fur increases the effect.   This is the theoretical pic-
ture of the explosion:
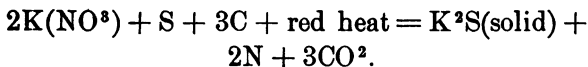
$$2K(NO^3) + S + 3C + \text{red heat} = K^2S(\text{solid}) + 2N + 3CO^2.$$

By weight

$$\underbrace{2(39 + 14 + 48)}_{202} + 32 + \underbrace{3 \times 12}_{36} = \underbrace{2 \times 39 + 32(\text{solid})}_{110}$$

$$+ 32 + 36 =$$

$$+ \underbrace{2 \times 14}_{28} + \underbrace{3(12 + 32)}_{132}$$

$$\begin{array}{lll}
KNO^3 = 202 = 74.81 \% & 75 & \text{potassium niter} \\
S \quad = 32 = 11.85 & 12 & \text{sulfur} \\
C \quad = 36 = 13.34 & 13 & \text{fine charcoal} \\
\hline
\quad\quad 270 \quad 100.00 &
\end{array}$$

On the second side of the equation stand

$$\begin{array}{lll}
K^2S \quad = 110 = \quad 40.70 \% \text{ (solid)} & 41 & \text{solid} \\
2N \quad = \quad 28 = \quad 10.40 \% \text{ gas} & 10 \\
3CO^2 = 132 = \quad 48.90 \% \text{ gas} & 49
\end{array} \Big\} \text{gas}$$

$$\quad\quad 270 \quad\quad 100.00.$$

59 per cent. of the powder is converted into gas.
One gram of the powder gives by the explosion 0.1
gram of nitrogen, 0.49 gram of carbon dioxyd.   At
0° C. and 760 mm., 0.001256 gram of nitrogen occu-

pies the space of one c.c.; 0.1 gram of nitrogen occu-
pies the space of 79.6 c.c.   0.001977 gram CO_2
occupies the space of 1 c.c.; 0.49 gram CO_2 the space
of 247.3 c.c.   The volume of gas produced by the
explosion of one gram of perfect black powder is at
0° C, 247.3 + 79.6 = 326.9 c.c.   One gram of best
powder, in small but perfect angular grains, occu-
pies the space of 0.9 c.c.; the surface of 1 c.c. being
six square centimeters.   Hence if one gram of such
powder be filled into a cartridge and a bullet be
pressed tightly upon the powder, a space will be
filled possessing six times $0.9 = 5.4$ square centi-
meters.   After explosion this same space will be
filled with 326.9 c.c. of gas which will press upon
the enclosing surface with $\dfrac{326.9}{0.9} = 363.2$ times the
pressure of the atmosphere or upon 1 square centi-
meter with $\dfrac{363.2}{5.4} = 67.26$ atmospheres.   But there
is another very important factor; the heat gener-
ated by the explosion, which expands the gas merci-
lessly, and if the enclosure be rigid, exerting an
ever-increasing pressure.   The gases expand, within
certain limits so nearly alike, that one coefficient
answers for all.   This coefficient is $\frac{1}{273}$ or 0.00367
volume for 1° C.   By the following reasoning we
arrive at the theoretical temperature produced by
the explosion of one gram of powder: 1 gram car-
bon through the oxydation into CO_2 produces heat
equal to 8050 calories (the heat would raise the
temperature t of 8050 grams of water by one de-

gree C.   Hence 0.13 gram of carbon will produce
$8050 \times 0.13 = 1046$ calories.   By the burning have
been produced 0.49 gram of CO_2, 0.1 gram of N and
0.41 of K_2S.   Each of these bodies has a capacity
for heat to be swallowed up before the heat can be
felt.   The temperature, the sensible heat, must
therefore be directly proportional to the absolute
heat—the 1046 calories, and inversely to the ab-
sorbed heat.   In a general way

$$T^o = \frac{A}{a}$$

in which A = absolute heat, a = weight of pro-
ducts into their respective specific heats.

   In our special case

$$T^o = \frac{1046}{0.499 \times 0.22 + 0.1 \times 0.24 + 0.41 \times 0.4}$$

$$T^o = \frac{1046}{0.108 + 0.024 + 0.164} = \frac{1046}{0.296} = 3534°C.$$

The a in the denominator is represented by the sum
of the products of the combustion of the powder;
each member multiplied by its factor representing
the unit of heat capacity or specific heat.

   Thus it is seen that by the combustion of one
gram of powder a temperature is generated equal to
3534° C., higher than that of an intense coal fire.
At this temperature the 326.9 c.c. of gas must have
expanded to $326.9 \times 0.00367 \times 3535 = 4236.6$ c.c.,
to 12.9 times their volume at 0° C., or 871.7 atmos-
pheres pressure per sq. cm., provided the law of ex-
pansion holds good at such high temperature, but

this is by no means certain. At any rate, the theoretical picture gives a measure for the actual phenomenon. We see that the pressure of the gas must be enormous, though less than the theoretical, in fact only about $\frac{1}{2}$ as shown by actual experiment, made for the military departments of several governments. Such experiments are known by the adjective *ballistic* (made with a ball). The reasons are several. In the first place the burning of the powder is never complete. 2. The reactions are not quite like the formula indicates. A part of the oxygen remains fixed by forming K_2SO_4, hence some of the carbon only burns to CO, whilst some of the nitrogen remains as NO. 3. The material of the apparatus—a gun for instance, or a mortar—is somewhat elastic.

As engineers we should know all that has here been given, to understand the effects of the blasting powder we use. I give you only the chemical facts connected with the matter.

Other powders. The white and smokeless powders all contain a nitric radical, either NO_2 or NO_3. In principle there is no difference between them and black powder. Their special compositions will be dealt with under the subject of carbon compounds.

INVESTIGATION OF THE BROWN FUMES OR NITROUS FUMES.

These always form, when $H(NO_3)$ acts upon an oxydizable substance, as copper for instance, or SO_2.

Acting with $H(NO_3)$ upon copper in a test-tube

we observe the tube filled with the brown fumes so long as the action continues. But if the tube be stoppered with a narrow tube for the escape of the gases, a different action ensues. We notice that the gas inside the tube turns lighter by degrees, at last being quite colorless, but at the mouth of the escape tube a steady cloud of dense, brown-colored gas is visible all the time. This at once suggests the presence of two different gases within the brown fumes. More precisely we would say: Through the action of HNO^3 upon an oxydizable body is generated a colorless gas—an oxyd of nitrogen. When this gaseous oxyd comes together with air the *brown gas* forms by combination of the air-oxygen with the colorless gas; but the brown gas itself must possess a ratio of oxygen to nitrogen *less* than 5/2, for if it is absorbed in ice water we find produced a mixture of *spirits of niter* and the *same* acid that was made by acting with H^2SO^4 on the residue left after heating niter. All this will be proved presently. The brown gas becomes colorless if mixed with an oxydizable body, as SO^2 for instance, evidently by loss of oxygen. Hence the *colorless gas* must have an oxygen to nitrogen ratio *less* than the brown gas.

Nitrogen dioxyd, NO^2 or N^2O^4, *hyponitric anhydrate* the *nitrous fumes.* Let the tube T, Fig. 47, be partly filled with dry lead nitrate and placed in furnace F. Make the U-tube U from a $\frac{1}{4}''$ tube, draw it out into a capillary at C, a and 6, then surround it in the basin B with a mixture of ice and coarse common salt; stick a thermometer t into the

mixture. If the salt be kept on snow or ice until
its temperature falls to 0° C., and if it be then mixed
with one volume of snow or fine-cut ice, the tem-
perature of the basin will drop to —20° C.   Make

FIG. 47.
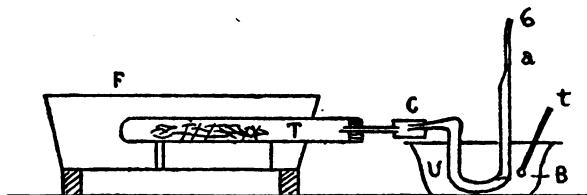
connection at C with T, and heat T to redness grad-
ually.   We know from previous experiment (com-
position of N^2O^5) that the $Pb(NO^3)^2$ breaks up into
PbO + brown fumes.   Thus

$$Pb(NO^3)^2 + heat = PbO + (N^mO^{p-x}) \text{ brown fumes}$$
$$+ (6—p—x—1)O.$$
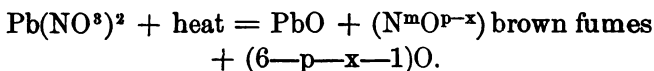
Passing into U the fumes condense into a brown
liquid and at *6* issues a gas which sustains combus-
tion with energy—(oxygen).   At end of decomposi-
tion close U at C and a with the blow-pipe.   If the
U-tube be changed twice, then you find in the third
tube colorless crystals.   These represent the true
substance.   The crystals melt at —12° C. to a color-
less or slightly yellow liquid.   It follows that no
crystals result if the temperature of the freezing
mixture be not at the least —15° C.   As the liquid
is heated by the warmth of the hand it becomes
more and more highly colored, giving out dense
brown fumes and reaches a constant boiling-point

at $+22°$ C. (in the hand, because the temperature
of the blood is $33°$ C.). On the addition of ice
water drop by drop, the liquid turns first green, then
blue, then colorless. It acts upon oxydizable bodies
more energetically than HNO^3, because the restrain-
ing bond of the hydrogen is removed. Mention has
already been made of the suffocating action of the
brown fumes. The living organism tries to avoid
the danger lurking in the breathing of the gas,
for the muscles of the epiglottis contract instantly
when the gas comes in contact with their nerve
ends. At Berlin, some years ago, fire broke out in
the yard of a large chemical works. Sixty carboys
of aqua fortis were stored under one shed. They
exploded, one by one. The acid flowing into the
straw and wood of the packing let out an immense
volume of brown fumes. Five of the firemen who
had been endeavoring to save the carboys, went
back to the station with the others, smoked a pipe
and went to sleep in their bunks. Within a few
hours they woke in convulsions and died shortly
after, in great agony. Let this be a warning to be
careful. Do not act upon metals, or sulfids with
HNO^3, except in a well-drawing hood; for even if
death does not ensue, there may be permanent in-
jury to the bronchiæ and their capillary ramification
in the lungs, from ulceration of the mucous mem-
brane. The composition of the brown gas we find
similarly to that of the lead niter. We make a small
U-tube U, Fig. 48, drawn out into capillary thread
at a, b. We take the weight and then fill into it a

few drops of the liquid, by pressure or by suction. In T there is the coil of copper wire. At B is the burette for measuring the gas, filled with solution Na(HO), and which is immersed in a dish of water

FIG. 48.
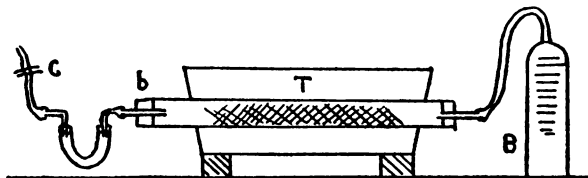
when in use. We fill the tube T with lime gas, insert U at b into the stopper and a into rubber tube leading to lime gas holder and furnished with clamps C; then connect the burette B. We bring T up to redness and turn on the lime gas in a gentle current. The radiant heat will suffice to volitalize the liquid oxyd of nitrogen and the lime gas will carry it over the copper gauze. Nitrogen and lime gas pass into B and the NaHO solution will absorb the lime gas. Thus we get the nitrogen volume which we deal with as in the previous experiment; w being weight of oxyd, n being the weight of nitrogen, w — n = O, the weight of the oxygen. Dividing n by 14 and w — n by 16, we get the ratio

$$\frac{n}{14} : \frac{w-n}{16} = 1 : 2 = NO^2 \text{ or } N^2O^4 \text{ or } N^4O^8$$

Some investigators claim the ratio N^4O^8 which can be interpreted as $N^2O^3.N^2O^5$ a combination of the two oxyds, on the ground that when ice water be

mixed with the liquid oxyd it breaks up into the two acid bodies: $H(NO^2)$, *hydrogen nitrite* and $H(NO^3)$, *hydrogen nitrate:* to wit

$$N^2O^3 + H^2O = 2H(NO)^2; N^2O^5 + H^2O = 2H(NO^3)$$
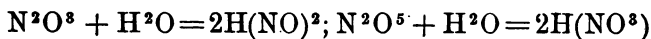
However, this view, which looks at the molecule as a *polymeric* molecule, *i. e.*, 4 times NO^2, only applies at low temperatures, for Dulong found for the brown gas the specific gravity 1.62, and this corresponds to

$$\frac{1}{2} \text{ vol. nitrogen} = 0.4856$$
$$1 \text{ vol. oxygen} = \underline{1.105}$$
$$\overline{1.5906}$$

so nearly 1.62 that we can have no doubt left.   The new gaseous molecule is surely $NO^2 = 2(\frac{1}{2}N + O)$. 1 vol. N + 2 vols. O = 3 vols., become 2 vols. NO^2; there is a condensation of 3:2 of $1\frac{1}{2}:1$.

When the brown fumes are passed into $H^2(SO^4)$, the fumes become absorbed, and if the operation be continued for a time, colorless crystals form in the acid.   The crystals are obtained more readily by pouring a few cubic centimeters of $H^2(SO^4)$ into a small flask and by spreading the liquid, through rotation, upon the entire glass surface.   If now the brown fumes are brought into the bottom of the flask, under the rotation the brown fumes become absorbed, a crystalline crust resembling ice forming all over the flask (inside).   The composition is not definitely settled, probably $2H^2(SO^4).NO^2$.   The reaction is of much economical importance in the manufacture of $H^2(SO^4)$ on a large scale and will be brought forward when we shall arrive at that process.

The colorless gas, nitrogen monoxyd, nitric oxyd, NO.
This body becomes generated whenever $H(NO^3)$ acts
upon oxydizable bodies, metals, metallic sulfids,
paper, wood, sulfur dioxyd. As soon as it comes
into contact with the air it changes into nitrogen
dioxyd NO^2 (brown nitric fumes). We obtain this
gas very pure by passing SO^2 into *warm HNO³ +*
water.

In flask *F*, Fig. 49, we generate SO^2 from the

FIG. 49.
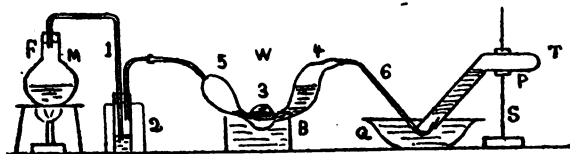
mixture *M*, which is copper gauze and H^2SO^4,
heated by a flame, according to equation

$$Cu + 2H^2(SO^4) = CuSO^4 + 2H^2O + SO^2.$$

Through tube *1* gas passes into the washing tube *2*,
partly filled with $H^2(SO^4)$ (moisture is retained and
flow of gas can be regulated). *W* is a so-called
Will's condenser, possessing the three bulbs, *3, 4, 5*,
and containing $2H(NO^3) + 2H^2O$. *B* is a basin
holding warm water to heat the $H(NO^3)$; through
tube *6* the gas can be delivered into any suitable
vessel. In the figure this vessel is a knee-tube *T*
filled with mercury and standing in mercury trough
Q. *T* is held by stand *S*. When the gas SO^2 bub-
bles into the $H(NO^3)$ it becomes oxydized into

$H^2(SO^4)$ and $H(NO^3)$ becomes changed into the nitrogen monoxyd.

Thus $3SO^2 + 2H(NO^3) + 2H^2O = 3H^2SO^4 + 2NO$ (colorless gas).
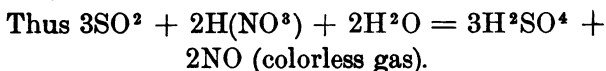
Do not think the composition of the gas must be NO, because the equation demands it, many students, and even some professors, have that belief. I wrote the equation because I know the gas to be NO. I could have balanced the equation in several other ways, merely by changing the coefficients of SO^2 and of HNO^3.

Proof of the composition of nitrogen monoxyd. Suppose we have allowed to enter into the knee-tube *T*, Fig. 49, about 10 c.c. of the gas and have marked this volume by a sticker. Banking upon the known maximum of affinity of potassium for oxygen, we will introduce, by means of a thin copper wire, a piece of metallic potassium at *P*, and heat the metal with a burner. A flash of light and a violent commotion of the gas accompany the act of deoxydation of the gas. I must hold the tube firmly, with the left hand, to prevent its being raised above the mercury level in *Q*. When the tube has resumed the temperature of surrounding air we find the volume of gas shrunk to exactly $\frac{1}{2}$; hence there is in one volume of nitrogen monoxyd $\frac{1}{2}$ vol. N $+ \frac{1}{2}$ vol. O or made into full units 1 vol. N $+ 1$ vol. O, the symbol of the gas is *NO*. There is no contraction in the union.

Specific gravity of NO found by weighing 1 vol. $= 1.0379$ (air $= 1$)

12

$$\frac{1}{2} \text{ vol. N} = 0.4856$$
$$\frac{1}{2} \text{ vol. O} = \underline{0.5525}$$
$$1.0381$$

Calculated specific gravity equal to the experimental, hence *NO* represents the *molecular volume* of the gas.

Properties of NO. The gas cannot occur in nature. Why? Because it changes to NO^2 on meeting the oxygen of the air. For the same reason we *do not know* whether it has odor or taste. Does not act on litmus paper. Its actions on the breathing organs are the same as those of NO^2, for the same reason as above. If the gas be conducted into a solution of copperas $Fe(SO^4) + 7H^2O$ or $Fe(Cl^2) + 2H^2O$ the solution turns *dark brown,* or even *inky black.* The gas is *completely absorbed.* Distinction from all other gases. This reaction enables us to recognize and identify a nitrate in an unknown mixture, even very minute quantities of the nitrate. Proceed as follows with this test: Bring the unknown solution (1 c.c.) into the bottom of a test-tube *T*, Fig. 50, add 2 c.c. of concentrated $H^2(SO^4)$ and mix. Then take into a glass tube *t*, which has been drawn out to a capillary, a strong solution of copperas (ferrous sulfate) $Fe(SO^4)$. Lower *t* into *T*, so that the point just touches surface of the liquid mixture, and let run out a few cubic centimeters. The two liquids are then unmixed, in two superimposed strata. Within a short time a dark ring will develop at the contact of the strata. If no dark ring develops then the unknown substance does *not contain any nitrate.*

The student should practice this reaction using as unknown a solution which was made up from one drop of strong $H(NO^3)$ and 50 c.c. of water (approximately 0.2 per cent. HNO^3).

Nitrites, Na(NO²), K(NO²), Ag(NO²). Di-nitrogen-trioxyd, N²O³. Both $Na(NO^3)$ and $K(NO^3)$ loose oxygen when heated at low red heat and more rapidly at bright red heat. Since neither the metal

Fig. 50.
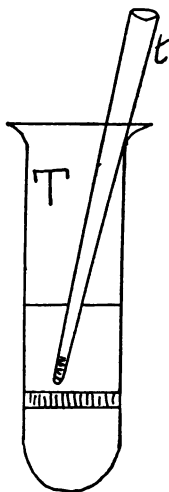
nor nitrogen is given off, the ratio between the three elements must become changed; a new body forms. This we can demonstrate readily in two ways: (1) by acting upon the residue with concentrated H^2SO^4 when copious brown fumes are given off; (Recall that the nitrates $+ H^2SO^4$ do not give

any fumes.) (2) by adding solution of $Ag(NO^3)$ to the water solution of the residue—a white precipitate falls out, which is not very soluble in water. This silver salt does not contain water, and by its decomposition we can find the ratio of Ag, N, O, by using the apparatus and method followed with the lead nitrate. Let the silver salt, which shall be named *silver nitrite* (note the substitution of the letter i for the letter a in nitrate) be $Ag(N^mO^{p-q})$ then we shall obtain by the decomposition

$Ag(N^mO^{p-q})$ + red heat = Ag + brown fumes.
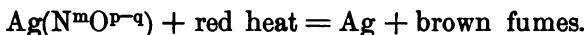
Let the fumes be decomposed by copper gauze at red heat and you get the nitrogen.

(N^mO^{p-q}) fumes + aCu + red heat = (p–q)CuO + (a–p–q)Cu + mN and thus we find :
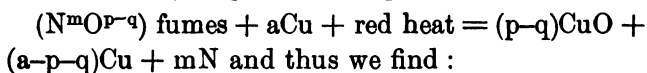
Ag : N : O = 1 : 1 : 2 hence the formula of the nitrite is

$Ag(NO^2)$ and similarly must be the Na, K salt
$Na(NO^2)$
$K(NO^2)$

The hydrogen salt cannot be made, it is *too unstable.*

Preparing $K(NO^2)$. Heat niter in an iron pot or crucible to melting heat, then add 2 parts of metallic lead for each part of niter. The affinity of lead for oxygen helps the decomposition of the niter :

$K(NO^3)$ + heat + Pb = $K(NO^2)$ + PbO
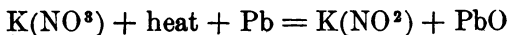
Molecular weight $K(NO^3)$ = 101, atomic weight of Pb = 207, hence 1 part niter + 2 parts lead, correspond to theory. In practice, however, the reactions are not complete. Some lead is apt to remain

unoxydized, some oxygen escapes, the residue is, usually, $K(NO^2)$ mixed with PbO, KNO^3 and K^2O. Dissolve the fused mass in little boiling water and let cool. The PbO will settle, the $K(NO^3)$ will crystallize. Decant (that is pour off) the liquid and evaporate to dryness, finally heat to melting and pour into pencil moulds, same as used for NaOH and KOH. $K(NO^2)$ is a reagent in use for the separation of cobalt from nickel, as well as for other operations. The salt usually shows an alkaline reaction from KOH, can be neutralized with dilute acetic acid.

In the nitrites, we have undoubtedly a peculiar oxyd of nitrogen. The radical (NO^2) is not that oxyd, its reactions are quite different. This oxyd is N^2O^3, for $K^2O.N^2O^3 = 2K(NO^2)^2$. This oxyd —*dinitrogen trioxyd*—is contained in the brown fumes, as gas. It may be condensed at—15° C. into a deeply blue liquid, which boils even at the freezing-point of water. *A blue solution* results from the action of NO gas upon a solution of $H(NO^3)$ in water (specific gravity $= 1.25$) *a green solution*, when the specific gravity is 1.35 (because this liquid then contains both N^2O^3 and $N^2O^4,(2NO^2)$. The same colors result when acids of the given specific gravities act upon certain oxidizable bodies. Any one not knowing this fact will often waste much time trying to find copper (blue nitrate) because he sees a blue solution, or chromium because he sees a green solution when acting on *galena*, the lead sulfid, for instance. The student should get this information by experiment to fasten it the more firmly.

If a solution of $Na(NO^3)$ or $K(NO^3)$ be shaken with amalgamated zinc (zinc coated with mercury) the solution will then contain *nitrite*, to be detected by the addition of the liquid to starch paste containing potassium iodid and some free H^2SO^4 (dilute). The paste turns *blue*, because

$$KI + H^2SO^4 \text{ (dilute)} + NaNO^2 = I + Na,K(SO^4) + H^2O + NO.$$
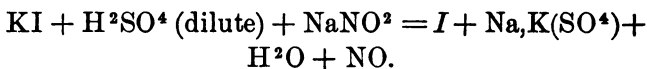
The rain water from a thunder shower will give this reaction, showing that it contains *nitrite;* azote and oxygen have become united by the electric discharges of the storm.

Dinitrogen monoxyd, N^2O, nitrous oxyd, laughing-gas. This gas arises when the monoxyd NO is allowed to stand in contact with easily oxydizable substances; finely divided zinc, iron filings, sulfites $(Na^2(SO^3))$, and many others. One-half of the oxygen is removed, or 2 molecules NO furnish one molecule N^2O.

Thus $2NO + Zn = N^2O + ZnO$

$\qquad 2NO + Na^2(SO^3) = N^2O + Na^2(SO^4)$.
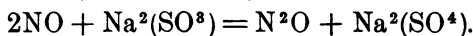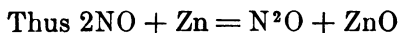
We proceed to prove this by acting with heated potassium upon the gas in a knee-tube, exactly as described for NO. The action is quite as energetic. After cooling the volume is the same as before the action. Hence one volume gas contains one volume nitrogen. Weight of one vol. gas (spec. gr.) $= 1.5270$
minus weight of one vol. N (spec.gr.) $\quad = 0.9713$
$$\overline{0.5557}$$

but 0.5557 is very near $\dfrac{1.1056}{2} = 0.5528 = \frac{1}{2}$ vol.

oxygen.

Hence the gas is $NO^{\frac{1}{2}}$ or N^2O.

The properties of the gas N^2O are remarkable. It was discovered by Priestly in 1776, and Sir H. Davy demonstrated its composition. The gas is colorless, possesses a faint sweetish taste and slight aromatic odor. One cubic centimeter at 0° C. weighs 0.001974 gram. The gas is quite soluble in cold water. At 0° C. one volume water absorbs 1.3 volumes of the gas, but at 20° C. only 0.67 volume. A taper burns in the gas more brightly than in air, almost as in oxygen gas. The gas can be taken into the lungs (breathed) without any discomfort. Quite on the contrary; its action when breathed, is that of a stimulant. The nerves become excited, the effect is similar to that of alcohol and ether—intoxication ensues, either numbness or acute mania. The effect is not by any means alike on all persons. Sir H. Davy gave it the name laughing-gas, pleasure gas. Its application in dentistry is well known. Dentists use it with nervous persons, who are unwilling to stand up against pain. Though not quite without danger, serious after-effects are less likely through its use than through other anæsthetics—ether or chloroform. The dentists buy the gas in the compressed state, in copper cylinders. At 0° C. the gas becomes liquid under a pressure of 30 atmospheres, that means when 30 volumes are compressed into the space of one volume, approximately; 300 litres of the gas yield 400 c.c. of liquid N^2O. When this liquid is allowed to evaporate it produces intense cold, like liquid air, and part of it becomes solid as

snow.   The liquid N^2O boils at $-89°$ C., and be-
comes solid at $-100°$ C.   For use of the dentists
the compression of the gas is only carried so far
that about 10 volumes are compressed into 1 vol-
ume; which means a pressure of 150 pounds per
square inch.

Preparation of the gas on manufacturing scale.   The
salt $NH.^4(NO^3)$, ammonium niter or nitrate, breaks
up into N^2O and H^2O when heated:

$$NH^4.(NO^3) + heat = N^2O + 2H^2O,$$
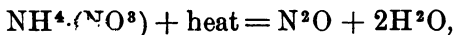
and thus furnishes an excellent raw material.   It

FIG. 51.
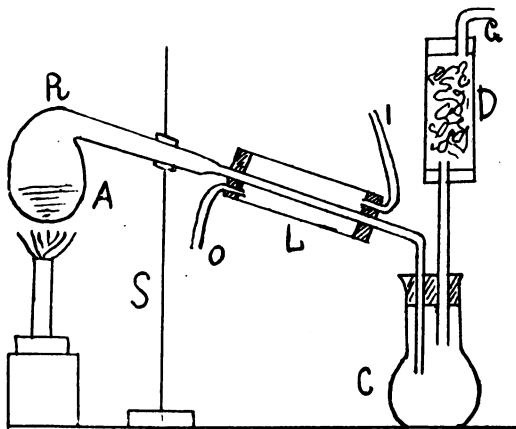
is not expensive.   Apparatus as shown in Fig. 51
will enable you to make the gas quickly.   *R* is a
small retort, into which has been put the ammonium
nitrate at *A*.   The stand *S* holds the retort.   *L* is a

Liebig condenser with the water inflow at i and its outflow at o. The condensed water and the gas separate in the flask C, the gas passes into the drying tube D and issues dry at G, whence it may be conducted into any desired holder, or to a compressing pump. Substitute large iron vessels for the small glass vessels and you have the manufacturing plant.

Recapitulation of the oxyds of nitrogen :

N^2O^5 (contained in the nitrates) does not exist in free state.

N^2O^4 (contained in the very unstable hyponitrates) brown fumes.

N^2O^3 (contained in the nitrites) blue liquid in free state.

N^2O^2 (forms no salts) originator of brown fumes.

N^2O (forms no salts) laughing-gas.

Nitrogen shows five different valences, from mono- to penta-valent, but all of them are weak. With other elements similar tendencies are observed, the smaller the affinity between two elements, the greater the number of combinations into which they enter.

CHAPTER XI.

AMMONIA, A VOLATILE ALKALI. A COMPLEX METALLIC RADICAL.

AMONG other facts concerning the action of KOH and NaOH, we gathered that these hydroxyds and their water solutions can dissolve zinc with the evolution of hydrogen; when the hydrogen is thus generated we say it is in the *nascent state*, meaning by this word (literally "being born") that there is a special force or energy connected with it, and which the gas has lost after it is once set free and allowed to collect or to dissipate. It is a play of the affinities. We observe that a solution of indigo is *not* decolorized by shaking it with hydrogen gas. Yet when zinc, dilute sulfuric acid and indigo are brought together, the liquid becomes colorless.

Blue indigo + Zn + H^2SO^4 + water = white indigo + $Zn(SO^4)$ + water. Hydrogen is not evolved until all the blue indigo is changed into white indigo, and we ascribe the change to *nascent* hydrogen. Thus also when niter, NaHO, and zinc act together, the escaping gas possesses not only a peculiar odor, but the gas turns *red* litmus to *blue*. There must be with the hydrogen a new *volatile* body which possesses the properties of the *alkaline hydroxyds*. Let this, as yet suspicious, body be named *ammonia*.

(186)

Passing the gas into water, the latter soon acquires *alkaline* reaction and the power to neutralize acids. If these neutralized acids be evaporated, crystals form, characteristic for each acid, the same as if those acids had been neutralized by KOH. Yet if these crystals be heated over an open flame, they will completely disappear, totally differing from any of the metallic salts. The total volatilization is proof that the body, which here takes the place of a metal, cannot contain either zinc or sodium, and since besides these, only the elements N, O, H had been in the generating solution, they alone can constitute the new body. Hydrogen we know to be a metal, because it takes the place of a metal in the salts, producing the hydrogen salts or acids. Oxygen and hydrogen together form water, which can take the place of a metallic oxyd, but not of a metal, hence we must conclude that the new body must contain nitrogen.

Investigation. The first step will be the preparation of a sufficient supply of the *ammonia gas.* A word about the name. We know that the name of the Egyptian sun god was *Rha Ammon;* also that the name of a powerful tribe of Bedouins in the desert to the southeast of the Dead Sea, in Palestine, was *Beni Ammon,* in Hebrew, the sons of Ammon, as we would say the sons of the sun. It is my belief that the name *ammonia* is connected in some way with Rha Ammon, though I cannot say how. The Egyptian priests must have known this body, and for its revivifying, penetrating odor likened it

to the effect of the sun's rays.   There is no histor-
ical record in existence to substantiate my view.
In the Latin translation of Geber's works (ninth
century A. D.) the name appears *sal armeniacum*,
which would mean the salt of Armenia, but that
stands also for rock salt.   I believe it is a mis-
spelling.

Preparation of ammonia.   Put into a 500 c.c. flask
(Fig. 52) 25 grams of NaOH, or about that much,

FIG. 52.
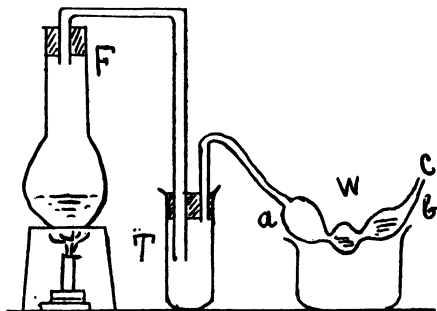
75 c.c. of water, 20 grams of zinc (in turnings), a
piece of bright sheet-iron, and 5 grams of niter.
Stopper the flask and connect by rubber tubing
with a Will's condenser.   The flask should stand
on a tripod upon wire gauze.   Heat gently and keep
up a slow evolution of gas.   The condenser is
charged with 20 c.c. of water and 5 c.c. of HCl con-
centrated.   It is best to place a tube, *T*, between
flask and condenser to receive any liquid spatter-
ings.   Will's condenser is especially adapted, be-

cause either of the bulbs, a, b, can hold more than the volume of liquid indicated, hence no danger of the running back of the liquid into T should a vacuum occur in F, nor a running out at C should the escape of gas become tumultuous at any time. The addition of some litmus to the liquid in W is advisable; so long as the color remains red we know that the liquid is still able to take up more ammonia. Any hydrogen mixed with the ammonia will escape at the point, C, of the condenser. The action must not be overhurried. In hurrying much more hydrogen escapes, doing no work. As soon as all the air is displaced from F, T, and W, you will note a tendency of the liquid in W to advance against the gas, to pass up into the bulb, a, an action which indicates the strong affinity between ammonia and HCl. It will take several hours to accomplish the complete change of the niter into ammonia. Towards the end it will be well to set T into a glass containing boiling water to drive out the ammonia from the liquid which may have been condensed in T. Then empty liquid from W into an evaporating dish, and evaporate over a water-bath. A white, granular residue will be obtained composed of cubic crystals like those of common salt, NaCl or KCl, which is another indication that ammonia must be a body similar to Na and K. We will name this white salt ammonium chlorid = Am.Cl. In the drug trade it is named *sal ammoniac*. Bringing this salt together with Na(OH) or K(OH) or Ca(HO)^2 we observe at once a pungent odor of ammonia.

$$K(OH) + Am.Cl = KCl + H^2O + Ammonia.$$

It follows from this action that there must be con-
tained in the salt *one hydrogen besides the ammonia.*
Important observation to be remembered.   Of the
three hydroxyds the one best servicable for making
ammonia is $Ca(HO)^2$.   Why?   Because it is a
powder.   Even better is the oxyd CaO, because if
an excess of it be added, then this excess will retain
the water in the form of $Ca(HO)^2$.   Even by rub-
bing together Am.Cl and CaO, ammonia is set free.
The process follows along the equation

$$2Am.Cl + 2CaO = CaCl^2 + 2 \ Ammonia + CaO.(H^2O)$$
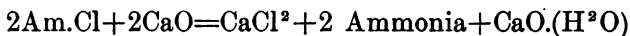
Pure dry ammonia gas results.

COMPOSITION OF AMMONIA.

Let the generating apparatus be set up as shown

FIG. 53.
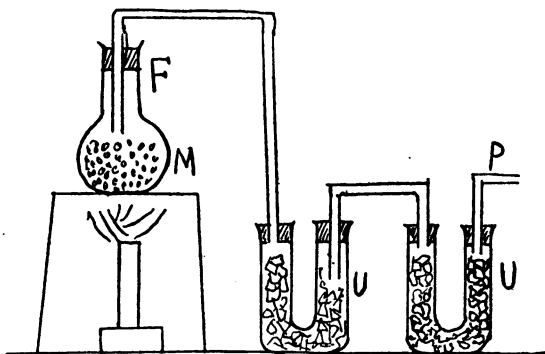
in Fig. 53.   In the small flask (not more than 100
c.c.) put the mixture M (4CaO+1AmCl) so that the

bulb is nearly full. To insure perfect dryness of
the gas, let it pass through two U-tubes U and U
both filled with pieces of burnt lime, pea size.

Proof that ammonia contains hydrogen. Rig a
hard glass tube T, $\frac{1}{4}''$ diameter, $12''$ long, as shown
in Fig. 54. Between two asbestus plugs b and b'
fill in coarse copper oxyd and ignite both asbestus
and oxyd thoroughly, before filling the tube. Let
the plugs be 3 to 4 inches apart. Arrange shield S so
that only the filled part becomes heated, the empty

FIG. 54.
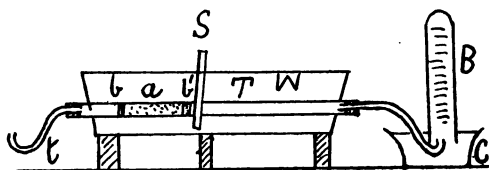
part projecting beyond the shield. Fill the tube
with ammonia gas by attaching t to P in Fig. 53.
Then heat a to redness, and let the gas pass slowly
(by heating generating bulb very gently). Soon we
see moisture appear in the cool tube at W. Mean-
while connect the outlet of T by means of a bent
tube with the test-tube B, which stands inverted in
basin C both filled with dilute $H^2(SO^4)$. Whatever
gas collects in B must be nitrogen (prove by its
negative actions), because any ammonia gas passing
out undecomposed will become absorbed by the
dilute acid. That the condensed moisture at W is
water we prove by bringing together with it a small
piece of potassium. But water could form only if
the ammonia contained *hydrogen*.

Proof that ammonia contains no oxygen. We re-place the copper oxyd at . *a*, Fig. 54, by a bright copper wire, or a strip of bright copper foil and repeat the experiment at red heat. The copper does *not cover itself with a film of oxyd.* This is proof of the absence of oxygen.

Hence ammonia must be

$$N^m H^p$$

Demonstration that the ratio, $\dfrac{m}{p} = \dfrac{1}{3}$. Let a small volume of the pure ammonia gas pass into the eudiometer *E*, Fig. 55, over *perfectly dry* mercury.
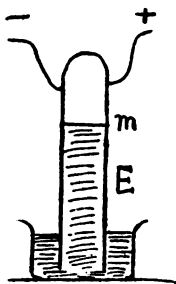
Fig. 55.	Fig. 56.
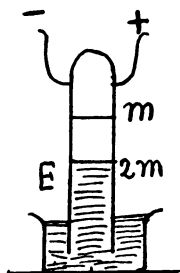
Dry the eudiometer, inside and outside, most thor-oughly, before filling in the dry mercury. A eudiometer is a glass tube open at one end, made of strong glass, either graduated or not graduated, but having . two thin platinum wires fused into the glass near the closed, or upper, end — +, so that an electric current of high potential may be sent across in form of a spark. Let *m* designate the portion of

the mercury meniscus after the ammonia gas has
entered.   Then turn on the current which has been
transformed to high potential by means of a Rhum-
korf coil.   We notice at once an increase in the
gas volume; rapid increase at first, but slowing
down by geometric progression until the maximum
enlargement of the volume has been reached at $2m$
as shown in Fig. 56.   The volume has doubled;
the hydrogen and nitrogen are now merely mixed to-
gether, the energy of the shocks from the sparks hav-
ing broken the chemical bond.   Now let us assume
that the entire volume of the gas be hydrogen, $i. e.$,
2 vols., let one vol. of pure oxygen be added, mak-
ing altogether 3 vols. of gas.   Let the spark pass
between the wires (under proper precautions, that is
covering the mercury trough with a towel and hold-
ing down eudiometer with the left hand).   Had our
assumption been correct there would now only be
contained in tube aqueous vapor and liquid water.
We must remove this water, because we started
with dry gas, by bringing into the gas a ball of
K(OH) fused to a thin, soft wire.   KOH absorbs
water eagerly.   A ball of fused $CaCl^2$ will answer
also.   We watch the gas from time to time and
remove the drying ball when the volume remains
constant for a full hour.   Since we know that
nitrogen will certainly be in the residue, we must
have a certain and unknown excess of oxygen after
the explosion, for we put oxygen equal to $\frac{1}{2}$ of the
total gas $H + N$.   Let this excess of oxygen $= dO$,
then the residue will be $= N + dO$.   Suppose we
     13

started with one vol. ammonia gas = 10 c.c. By decomposition this became = 20 c.c. By addition of one vol. of oxygen = 10 c.c. this became = 30 c.c. Now we explode the mixture and remove aqueous vapor, and find that 30 c.c. have shrunk to 7.5 c.c. Then 30 — 7.5 c.c. = 22.5 c.c. here disappeared in form of H^2O; $\frac{2}{3}$ of this contraction was hydrogen, $\frac{1}{3}$ oxygen.

$$\frac{2 \times 22.5}{3} = 15 \text{ c.c. of H}$$

$$\frac{22.5}{3} = 7.5 \text{ c.c. of O}$$

But we had used 10 c.c. of O, hence d O = 10 — 7.5 = 2.5; hence N + d O = N + 2.5 = 7.5 (gas volume after explosion); N = 7.5 — 2.5 = 5 c.c.; hence ratio $\frac{n}{p} = \frac{5}{15} = \frac{1}{3}$. The formula of ammonia is H^3N. Into 10 c.c. of H^3N are compressed 15 c.c. H + 5 c.c. N. Into 1 c.c. of H^3N are compressed 1.5 H + 0.5 N, or *two* volumes are condensed into one.

1½ vols. hydrogen weigh gram . . . 0.1038
½ vol. nitrogen weighs gram . . . 0.4856
_____
0.5894

which is the calculated specific gravity or *volume weight* of ammonia, and agrees fairly well with the experimental specific gravity of 0.596. The *molecular weight* (H = 1) is 14 + 3 = 17.

The chemical nature of ammonia—ammonium. Ammonia gas is easily absorbed by water. 1 c.c. of water at 0° C. will absorb 1050 c.c. of the gas;

much heat is produced by the absorption.   The re-
sulting liquid, be it concentrated or dilute, has the
same pungent odor as the gas.   The liquid possesses
the *biting taste* of potassium and sodium hydrates.
Raises a blister on the tongue or lips.   The liquid
is lighter than water; at $+ 14°$ C. its specific gravity
is 0.8844, and contains 35.0 per cent. of NH^3.   This
liquid goes in the drug trade by the name *aqua am-
monia* or *ammonia water*.   We chemists call it *ammo-
nium hydrate*.   Because from the actions of this
liquid towards the acids, we conclude that as soon
as the gas, NH^3, comes together with water it com-
bines with the latter, thus

$$NH^3 + H^2O = (NH^4)(HO) = \text{\textit{ammonium hydroxyd.}}$$

One hydrogen leaves H^2O, and attaching itself to
NH^3 brings forth the *metallic radical* (*NH⁴*).   Here-
tofore we have only had non-metallic complex rad-
icals, such as (SO^4), (NO^3).   This radical, (NH^4),
we name *ammonium*.   Note carefully the difference
in the words ammonia and ammonium, and try not
to confound them in your speech.   Ammonia is the
real, actual compound, NH^3; ammonium the hypo-
thetical metal, NH^4.   I say hypothetical because
we have no means at present to isolate it; in at-
tempting to tear (NH^4) from (HO) we always get
$NH^3 + H^2O = $ ammonia $+$ water.   And yet there
is no unproven assumption in chemistry more cer-
tain than this, that ammonium would show all the
physical characters of a metal if we could separate
and condense it, even as hydrogen itself would do.

Indirect or circumstantial proof of the ammonium theory.   Let us introduce (Fig. 57) into the tube, *T*, over mercury, one volume of dry HCl and one volume of dry NH^3.   The one gas is strongly acid, the other strongly alkaline.   In order to get the volumes equal let *t* be a small tube holding 10 c.c. up to the mark *m*.   If *t* be filled with mercury and then held so that the upper rim of the sticker falls together with the level of the mercury in the trough,

FIG. 57.
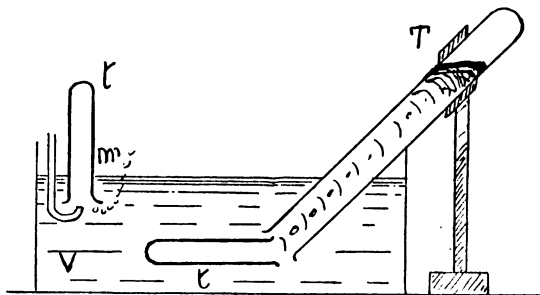
V, and if now the gas-delivery tube be brought under the rim and the gas allowed to enter until all the mercury is displaced, that is, until the bubbles come up on the outside, and if we do the same with the other gas, then we have measured the gases exactly at the same pressure and temperature.   For the transmission of the gas from *t* into *T* we incline *T* as much as possible, and then with the left hand *t* is inclined in the opposite direction, the open end of *t* shoved under the open end of *T ;* the closed end of *t* is then pressed down, and the entire volume of gas

passes above the mercury into T. When the two gases meet a white cloud forms; the mercury rises and occupies practically the whole of T. Both gases have disappeared, no hydrogen has been liberated, we have

$HCl + NH^3 = HCl.NH^3$, (sal ammoniac.)

But the resulting body is a white salt crystallized in cubes and octahedrons, or a combination of the two, exactly the same as KCl and NaCl. By action of H^2SO^4 upon this salt we obtain HCl, as we did from NaCl and KCl. Hence we deduce that a body must be in the salt, in every respect equal to either sodium or potassium. That is ammonium, NH^4.

$HCl.NH^3 = (NH^4).Cl = AmCl.$

Some chemists always write Am. instead of (NH^4) in order to lay stress upon the metallic nature of the group (NH^4). Because one volume HCl combines with one volume NH^3 we say ammonium is a monad, a monovalent radical; hence there is

one nitrate $(NH^4).(NO^3)$

two sulfates $\begin{cases} (NH^4).H.(SO^4) \text{ acid sulfate, bisulfate} \\ (NH^4)^2.(SO^4) \text{ neutral sulfate} \end{cases}$

one chlorid $(NH^4).Cl.$

Knowing now the composition and nature of ammonia and ammonium, we can write the equation of its formation from $Na(OH)$, Zn, $Na(NO^3)$, or $K(NO^3)$ thus, in two stages,

(1) $2Na(OH) + Zn = Na^2ZnO^2 + 2H$

(2) $2Na(NO^3) + 16H = Na^2O + 5H^2O + 2NH^3$

or $16Na(OH) + 8Zn + 2Na(NO^3) + $ water $= 2NH^3 +$
     $8Na^2ZnO^2 + 4H^2O + 2Na(OH)$

or $8Na(OH) + 4Zn + Na(NO^3) + $ water $= NH^3 +$
     $4Na^2ZnO^2 + Na(OH) + 2H^2O.$
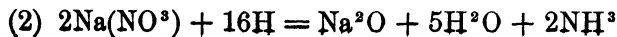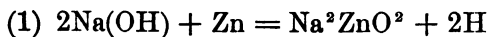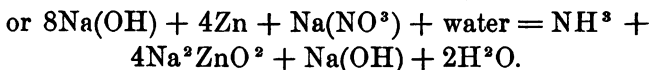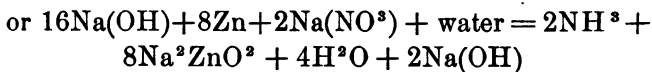
The incentive for the action is the tendency of the zinc and sodium to form the salt Na^2ZnO^2 (sodium zincate), then the hydrogen in the *nascent state* attacks the niter, substitutes itself for the oxygen and changes the latter into H^2O. A very similar action takes place when zinc is in presence of dilute H^2SO^4 and $H(NO^3)$. Here the incentive lies in the tendency of zinc to displace the hydrogen in H^2SO^4 and to form $Zn(SO^4)$. Then the nascent hydrogen will attack HNO^3 as in the alkaline solution. Thus:

$$9H^2SO^4 + 8Zn + 2HNO^3 + \text{much water} =$$
$$8ZnSO^4 + (NH^3)^2H^2SO^4 + 6H^2O.$$
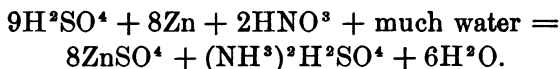
It also follows that a similar action will take place when zinc acts upon a very dilute water-solution of $H(NO^3)$ itself, but in this case only part of the nitrogen becomes changed into NH^3.

Thus $10H.(NO^3) + 4Zn + $ water $= 4Zn(NO^3)^2 +$
     $NH^3.HNO^3 + 3H^2O.$
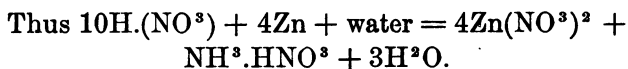
Of 9 molecules $H(NO^3)$ only *one* becomes changed into NH^3. The student must practice on these equations specially, because on them depends a method, and a very good one it is, to determine in an unknown substance the percentage of nitrate and nitrite. For it is evident that the action must be similar upon nitrites; one molecule of nitrite requires 2H less for its conversion into NH^3. Besides

these, which we may designate as inorganic or mineral processes, there are many other processes by which ammonia is generated, namely the processes of *fermentation* and *putrefaction* ; the latter process is only a variety of fermentation and often referred to as putrid, or stinking, fermentation.   1. Ammonia forms in the curing of tobacco.   The air-dry leaves being made into piles, soon begin to feel warm and give out a strong odor of ammonia.   The nicotin of the leaf which contains much nitrogen is broken up by the ferment (a fungus) and the tobacco looses its rankness.   The chemical reactions are complex and could not be understood by you at your present state of knowledge.   2. Ammonia forms in the fermentation of urine, because this secretion contains much urea—a highly nitrogenous substance like nicotine.   3. Ammonia forms in the distillation of soft coal ; because the coal contains from one to two per cent. of nitrogen ; and although one can only get—say 20 lbs. at most—of ammonium sulfate, by bringing the gases from the distillation in contact with H_2SO_4, yet so many millions of tons of coal are distilled every year, that the total of ammonium sulfate is enormous, and constitutes in fact the only *commercially important* source of supply of ammonia.   The great bulk of this goes back to the field as fertilizer, to supply the growing crops with nitrogen.   Much is however consumed chemically in the arts and manufactures.   Though not immediately a subject for the miner or metallurgist, yet every engineer ought to be acquainted with these short statements.

Ammonia combines with many bodies, among others with silver chlorid and calcium chlorid. Note this, so that you do not attempt to dry the gas by passing through $CaCl^2$. On the other hand, we may utilize this fact to procure *liquid NH³* (not ammonia water). AgCl is better suited than $CaCl^2$. Bring the dried, pulverized AgCl into a tube and pass over it, slowly, dry NH³ so long as the latter is absorbed. Then bend a strong glass tube F into a knee Fig. 58, and pour the AgCl.NH³ into this tube. Clean the tube at d and draw it out over the lamp, making a good strong job. The tube will be then as shown at a in Fig. 58. The AgCl.NH³ lies at

FIG. 58.
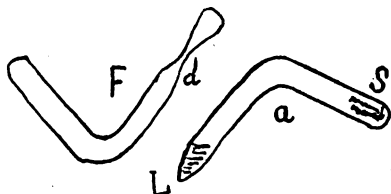
S. Immerse the pointed end into snow or ice and heat S slowly. Soon a colorless, very mobile liquid will condense at $L;$ this is liquid NH³. The liquefaction is, in this case, produced by the self-pressure of the gas as it becomes expelled at S. If allowed to stand the liquid will disappear because the AgCl has once again taken up NH³. The experiment may be repeated over and over. At —40° C. the gas becomes liquid without any extra pressure. At —90° C. the liquid turns into a snow-

white solid, which melts at —75° C. and has no odor, owing to the absence of tension at this low temperature. The tension of liquid NH^3 at 0° C. is 7 atmospheres, and its specific gravity $= 0.63$ (water $= 1$).

In the chemical factories aqua ammonia or ammonium hydrate is prepared from $(NH^4)^2SO^4$ by means of milk of lime in large iron cylinders C, Fig. 59.

$(NH^4)^2SO^4 + Ca(HO)^2 + \text{water} + \text{heat} = 2NH^3 + Ca(SO^4) + 2H^2O + \text{water}$.   It is necessary to keep

FIG. 59.
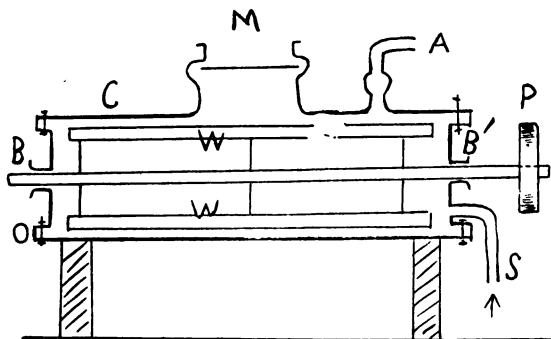
the mixture in constant motion by means of a stirring wheel W, the shaft of which passes through well tightened stuffing boxes $B\ B'$. The manhole M serves to introduce materials; the live steam enters at S; the ammonia gas together with a certain quantity of water vapor passed out at A. O is the discharge opening, and the pulley P transmits the power to the wheel W.   From A the gas passes

through a cooler in which the aqueous vapor also
condenses and flows partly as gas, partly as highly
concentrated liquid into glass balloons (carboys), or
iron cylinders if the liquid is to be shipped into hot
climates.   The carboys must be most carefully
packed in straw or salt hay, for if a carboy should
break, the hold of a ship—for instance—could not
be entered; the gas is deadly, causing immediate
suffocation.

The concentrated aqua ammonia is much used in
the Carré ice machine, the construction of which is
explained in physics.   Its principle is that a con-
centrated solution of ammonia gives out $\frac{1}{4}$ its NH_3
as gas, without any water, when gently heated. If
the gas be taken by a suitable pump and forced
into a strong tube, which is cooled by running
water, so as to remove the heat of compression, and
if the compressed gas be allowed to flow into an-
other tube which is surrounded by water—stagnant
—then this water will fall below its freezing-point,
it will become ice. Why? Because the compressed
gas in expanding into the tube (from which the air
has been pumped) will absorb the heat necessary
for its expansion from the surrounding objects.
Theoretically no ammonia is lost, because the ex-
panded gas is again taken hold of by the pump and
compressed as before.   Practically a certain portion
is lost through unavoidable leakage of the appara-
tus, and must be replenished.

The aqua ammonia also serves as raw material
for the preparation or manufacture of the other

salts, the *nitrate* (for the manufacture of laughing
gas), the *chlorid* (sal ammoniac), the *carbonate* and
the *bicarbonate.* The latter salts are also known as
hartshorn salt, because they were formerly obtained
by distilling hartshorn or other kinds of horn. It
has been mentioned that horn and skin as well as
hair are so-called *albumenoid* bodies (like albumen
—white of egg) containing from 15 per cent. to 17
per cent. of nitrogen. Now if the horn be heated
in a closed vessel, it will char and give off fumes as
well as gases. Amongst these is the *ammonium car-
bonate*, and it may be condensed.

Both carbonate and bicarbonate evaporate in the
air, giving a strong odor of ammonia, hence known
as *volatile salt, smelling salts*, to be applied to fainting
persons. Owing to their easy and complete volatili-
zation, these salts are used instead of baking soda
in the making of fine cake. Being incorporated
into the dough (flour, milk, sugar, eggs), the salt
becomes gas in the oven, raises the dough, and
leaves neither taste nor smell.

$(NH^4)^2CO^3$ = normal or neutral carbonate.

$H^2O.(NH^4)^2CO^3.CO^2$ = bicarbonate.

The *neutral* $(NH^4)^2CO^3$ is a highly unstable salt.
As soon as heat is applied it breaks up. The trans-
parent or translucent crusts which we buy as neu-
tral carbonate have normally the composition :

$2((NH^4)^2CO^3).H^2CO^3$ = sesquicarbonate, or $1\frac{1}{2}$
carbonate.

The salt is made by heating together in an iron
retort ;

$(NH^4)^2SO^4 + CaCO^3$ (chalk) or $(NH^4)Cl + CaCO^3$. The bicarbonate is usually a granular substance, but may easily be obtained in long prismatic, ortho-rhombic crystals, white or colorless. Composition as above, $(NH^4)^2.CO^3.H^2CO^3$.

It is prepared by passing lime-gas into a saturated solution of the sesquicarbonate. Being less soluble than the latter salt, the bicarbonate falls out in grains.

Sal ammoniac, ammonium chlorid, $(NH^4).Cl$. A white or colorless salt. Sometimes a loose, fluffy

FIG. 60.
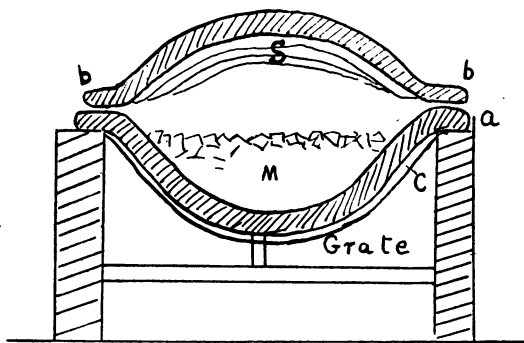
powder composed of small cubic crystals. Mostly in lumpy crusts, dense, as if they had been melted, and exceedingly fibrous, tough; will not grind into powder. To study the formation of this body, place two watch glasses alongside of each other, pour into the one concentrated HCl, into the other concentrated aqua ammonia, and cover the two with an

inverted beaker glass or bell jar.   Both liquids giv-
ing out gas, there will be at once a white cloud.
The glass and table cover themselves with snowy
sal ammoniac, feathered and fern-like aggregates of
small crystals.   At the point of sublimation or vol-
atilization the salt breaks up into $HCl + NH^3$.   One
smells both at the same time, but so soon as the
temperature drops reunion ensues, hence the salt
can be sublimated in earthenware vessels, glazed, to
avoid yellow stains.   In Fig. 60, a is earthenware,
b is earthenware, c is a cast-iron vessel into which the
vessel, a, fits, M is the crude salt, and S represents
the sublimated crusts of the salt.

   Use of sal ammoniac in soldering.   Soldering means
the joining together of two metal surfaces by means
of a film of liquid metal (solder) whose melting-
point is much lower than the melting-point of the
metals which are to be joined.   Solder is either
hard or *soft*.   Hard solder is an alloy of 2 pts. lead
and 1 pt. tin ; soft solder contains one lead, one tin.
The soldering-hammer or iron is a pointed piece of
copper, the point of which is coated with tin.   Tin
will not stick to heated copper, because the latter
covers itself with a film of oxyd, as you well know.
But if the hot copper be rubbed together with the
tin and sal ammoniac, then the two metals will cling
together ; the tin fairly jumps at the copper.   Why?
Because we have seen that the $(NH^4).Cl$ when
heated breaks up into $HCl + NH^3$.   But HCl at
once converts the oxyd film into fusible chlorids,
Cu^2Cl^2 ; the metals become bright and join.   After

the hammer is well tinned it will hold liquid solder. And if now $(NH^4)Cl$ in powder be strewn over the surfaces which are to be joined (brass for instance) the $(NH^4)Cl$ will cleanse them, the solder will adhere. Liquid HCl or hydrochloric acid may be used, but is inconvenient and not so effective, because it evaporates too rapidly. Sal ammoniac is used in medicine, and also for freezing mixtures, because its solution in water absorbs much heat.

SOLVAY PROCESS.

The Solvay process, also known as the ammonia-soda process, has become of such great importance that we must know something about it. Nearly one-half of the world's supply of soda-ash is now manufactured by this method. Like many other processes, the reactions underlying it were known many years before the mechanical difficulties of applying them could be overcome. The reactions involved here are

$NH^3 + H^2O + CO^2 = NH^4HCO^3.$

$NaCl + NH^4HCO^3 = NaHCO^3 + NH^4Cl.$

$2NaHCO^3 + heat = Na^2CO^3 + H^2O + CO^2.$

$CaCO^3 + heat = CaO + CO^2.$

$2NH^4Cl + CaO = CaCl^2 + 2NH^3 + H^2O.$
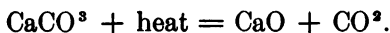
The last two equations show the uses made of by-products, which help to make the process a commercial success.

The equations represent the following operations:
1. The formation of NH^4HCO^3, which immediately

reacts with NaCl, producing the most insoluble combination possible, when CO_2 is passed into purified ammoniacal brine.   2. The calcination of the $NaHCO_3$ to form the normal carbonate, Na_2CO_3.   3. The decomposition of limestone in a lime kiln to produce CaO for by-product recovery, and CO_2 for operation 1.   4. The recovery of ammonia to be used over again.

The initial supply of NH_3 is obtained from compounds that are the by-products of the coal-gas works.   Ammonium sulphate is the principle compound used.   From the equations one might think that only the initial supply of NH_3 would be needed for continuous operation ; but leakages have to be made up from an outside source.

The CO_2 is obtained from the lime kilns and also from the calcination of the bicarbonate, $NaHCO_3$. The lime-kiln gases are produced in continuous kilns, and are cooled and purified before being passed to the carbonating towers.   These gases contain about 35 per cent. of CO_2.

The purified brine is first saturated with NH_3, the heat produced being taken up by cooling coils in the tank.   The ammoniacal brine is then pumped into towers, supplied with perforated diaphragms to make good contact between the liquid and the CO_2 which is forced in under pressure.

The milky liquid drawn out from the bottom of the towers contains the $NaHCO_3$ in suspension. This is separated and washed by means of centrifugal machines.

The bicarbonate is then calcined in covered cast-iron ovens to produce the Na_2CO_3, soda-ash. The gaseous products are cooled and sent back to be used again. The soda-ash produced by this process is more fluffy than the Leblanc soda-ash, hence it is often recalcined to increase its density. Ordinarily the Solvay soda-ash is exceptionally pure.

CHAPTER XII.

ORIGIN AND OCCURRENCE OF NITER.

ALL nitrates being easily soluble in water, we can expect to find any of them as mineral only under exceptional conditions; that is, in places protected against water. Such conditions exist in the rainless parts of North America and South America, Asia, and Africa. Europe has no rainless districts. But the Continent of Australia might yet prove to be a storehouse of niter; it is hardly explored as yet. Nitrates or any nitrogen compounds have never yet been found among the rock-forming minerals. Thus we are forced to the conclusion that the *air* contains the entire supply of nitrogen from which plants draw this element; store it in their structure first as *protoplasm*, then by differentiation into more complex tissues and combinations as the *gluten* of the cereal seeds, as *nicotine* in tobacco, as *morphine* in the poppies and multitudes of others. The animals feed upon the plants, building up still more complex tissues, such as muscles, nerves, skin, hair. These in their turn become metamorphosed, changed into matters rejected or excreted. Where animals congregate in numbers, as in cattle-yards, stables, etc., one notices the soil reeking with ammonia and ammonium carbonate

14   (209)

from the fermentation of the excreta. Before long
a white film appears upon the surface (when dry
weather sets in): the white film is made up of small
prismatic crystals of *niter*. Hence we conclude that
ammonia and ammonium carbonate become oxy-
dized in the presence of a sufficiency of an alkaline
body—become nitrates. If the niter film be scraped
off from time to time, the raw material for the
manufacture of niter is given in these scrapings. It
will only be necessary to extract this niter earth
with water, strain the liquid through cotton or linen
cloth, and evaporate to the point of crystallization
and let cool, when the nitrate will form in large
crystals, mostly colored yellow and known as *crude
niter*. By resolution and crystallization, at the last,
pure niter results. Through this method fully one-
third of the niter of commerce is still at this time
made in India, notably in the valley of the Ganges
in the Kingdom of Bengal. By piling up soil rich
in humus into heaps or walls, 3 to 4 feet deep and
6 feet high, and covering these heaps with a shed, a
so-called *niter plantation* can be built. A system of
gutters or pipes distributes the liquid animal excre-
tion—urine—over the tops of the heaps, wood ashes
are strewn over from time to time (to supply the
potassium), and before long the white niter film will
appear on the *wind face* of the heaps. It is scraped
off regularly ; the extracted earth being always re-
turned to the heap, and thus a continuous process of
niter-production becomes instituted. Likewise the
earth floor of stables was dug up from time to time

in all the villages of France and the rest of the continent of Europe during the Napoleonic wars, to supply the niter for the enormous consumption of gunpowder.   Sweden is the only country where this custom still prevails.

However, the discovery of an extended territory in Peru, under the surface of which lies a natural deposit of *soda niter*, has gradually produced a thorough revolution in the niter industry.   The former Peruvian Province, Tarapacca, now belonging to Chili, is formed by a plateau with an average alti-

FIG. 61.
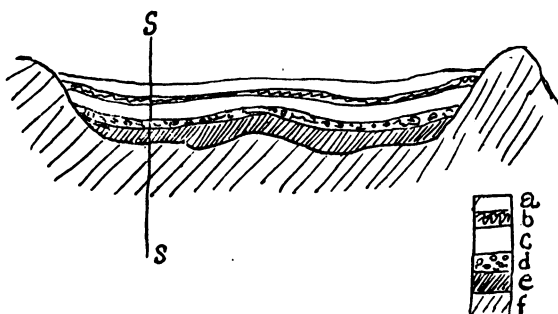
tude of 3,000 feet.   It forms the first steps, so to speak of the giant stairway of the Andes, the highest step of which is 26,000 feet.   The surface rocks are all of volcanic origin, being both basalt, porphyry and trachyte.   Between ridges of these rocks extend flat basins whose surfaces are destitute of vegetation except a few plants which have become acclimated. The region is quite *rainless*, a perfect desert.   Fig.

61 is a section through a niter basin. *s, s* gives a vertical section of the different layers; *a*, top layer of ashy gray sand and pebbles, *b*, conglomerate in which the same material contained in the top layer is cemented together with clay and salt, *c*, *massive niter*, sometimes 8 to 9 ft. thick and perfectly white, a mixture of sodium nitrate, sodium chlorid, potassium sulfate, sodium sulfate, *sodium iodid*, sodium iodate with more or less fine sand and clay, *d*, pure sodium chlorid (common salt), *e*, clay and loam, *f*, bed rock-granite, porphyry, basalt. The natives give to the niter the name *caliche*. The mining operations consist in sinking bore holes to the surface of bed *e*, the clay. The diameter of the hole admits a workman of small stature, who widens out a small chamber and charges it with 500 to 600 lbs. of powder or a corresponding quantity of dynamite. The hole is then filled first with dry, then on top with wet, sand. The explosion usually breaks up the niter bed in a circle of about 90 to 100 feet in diameter. The niter blocks are then sorted out and transported to the leaching works some distance away. In 1873 the niter bed was estimated to underlie a territory of 550 square miles, and each square mile to contain about four million tons of niter, which would give a total of 2,200 millions of tons or an annual yield of two million tons for a thousand years. But since the present consumption is about ten million tons per year, the enormous deposit will not last over 200 years. How came this deposit to be? The nitrogen must have been

brought by the instrumentality of either plants or animals or both; our present knowledge admits of no other source.   As we find the Chincha Islands just off the coast of Peru, and upon these islands millions and millions of tons of *guano*, Indian word for the excrements of birds, it has been suggested by some that this depression or gap in the Andean Mountain chain was used in past ages as the transition point for the east-west migration of birds and they made a halting place on the shores of existing lakes (now dry desert).   This theory, while accounting for the nitrogen, leaves out the phosphate contained in the guano.   There are no phosphates in the niter beds; phosphates are much less soluble than the nitrate of sodium; they would surely be found with the niter if guano had been the source of the nitrogen.   Equally fallacious is the theory of sea-weeds as original nitrogenous material.   " We do not know ! " remains as answer.

CONVERSION OF SODA NITER INTO POTASH NITER.

Although $Na(NO^3)$ contains more (NO^3) per unit weight than $K(NO^3)$, $Na(NO^3)$ being 85, KNO^3 being 101, yet experiments proved the unsuitability of $Na(NO^3)$ for gun powder.   Thus the conversion of $Na(NO^3)$ into $K(NO^3)$ became necessary.   It is readily done by the reaction

$$Na(NO^3) + KCl = K(NO^3) + NaCl.$$
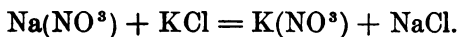
$Na(NO^3)$ is produced in Chili, KCl is produced (see under potassium) in the salt mines at Stassfurt, Germany.   Conversion comprises the following

stages or operations: (1) Dissolve the soda niter in
1.5 parts of boiling water in a large iron vessel or
open boiler, B (Fig. 62). (2) Dissolve KCl in three
parts of water. (3) Hang into B a perforated sheet-
iron vessel, P, by means of chain, $C\ C$, and a crane.
(4) Add the KCl to the boiling $Na(NO^3)$ solution in
quantity corresponding to the ratio niter $= 85$,
KCl $= 74.5$. (5) Common salt, NaCl, will begin to

Fig. 62.
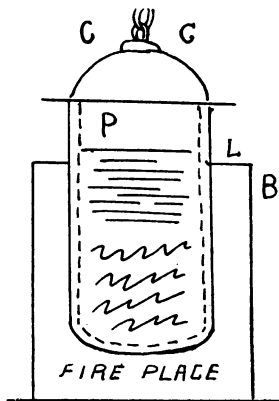
fall out at once as a fine, granular body, because it
is less soluble in the given water than either of the
two others. (6) NaCl crystals will collect in the
perforated or basket vessel, P, more and more as the
liquid is boiled away to one-half. (7) The vessel,
P, is lifted out and washed with boiling water,
which displaces the adhering niter liquor. The
washings are boiled down and added to liquid in B.
This liquid is run into shallow iron pans, where the

impure $K(NO^3)$ now comes out as a massive crystal crust as the liquid cools down. (8) The mother liquor, being chiefly NaCl with some $K(NO^3)$, is boiled down, the salt falling into basket as at first. (9) The massive, impure $K(NO^3)$ is redissolved and boiled down until no NaCl falls,. and is then run into vats, where it cools under constant agitation. The agitation causes the niter to fall out in small, loose crystals like granulated sugar. The niter meal is raked and dipped out, thrown upon drying floors, and then packed into bags and shipped. After this refining process the niter still holds about one-half per cent. of NaCl, which does not, however, interfere with its further use in powder making. The NaCl produced by this process is chiefly used for pickling meat, as the small quantity of adhering niter is desirable as a better preserving agent even than the salt.

CHAPTER XIII.

THE MANUFACTURE OF HYDROGEN SULFATE OR SULFURIC ACID ON A COMMERCIAL SCALE.

1. *Direct proof that H^2SO^4 results by the union of SO^3 with H^2O.* Sulfur disappears when heated with concentrated HNO^3. It disappears easier if HCl is also present. If the liquid be then evaporated on a water-bath a point will be reached when no further evaporation takes place. Water must be added several times and the liquid evaporated to get rid of HCl and excess of HNO^3. The residue has all the characters of hydrogen sulfate. Let the action be made with a known weight of the flowers of sulfur, say 0.5 gram. Then let us add water, after the evaporation and also 3 grams of pure lead oxyd (PbO), and let everything be transferred to a clean porcelain crucible of known weight, and be evaporated to dryness. We know that lead vitriol will stand a low red heat without decomposition, and also that lead nitrate decomposes below red heat into $PbO + 2NO^2 + O^2$. If then we heat the crucible to redness until the weight be constant, we shall have the total 3 grams of lead oxyd, the total 0.5 gram of sulfur and the oxygen which was taken up by the sulfur to form the hydrogen sulfate, but

(216)

there will be no water, because PbO has displaced the water in $H_2O.SO_3$ forming $PbO.SO_3$.

We find, after ignition, that the contents of the crucible weigh 4.25 grams; 0.75 gram of oxygen has been taken up by 0.5 sulfur, for $4.25 - 3.0 - 0.5 = 0.75$; hence $\frac{0.5}{32} : \frac{0.75}{16} = 0.01563 : 0.0463 = 1 : 3$, hence SO_3. The reaction between sulfur and hydrogen nitrate alone is: $S + 2H(NO_3) + \text{heat} = H_2O + SO_3 + 2NO = H_2(SO_4) + 2NO$. (The HCl when added acts as a catalyzer possibly through the momentary formation of a chlorid of S.) Thus 32 lbs. of S will yield with 126 lbs. of $H(NO_3)$, 98 lbs. of $H_2(SO_4)$. Value of 1 lb. S $= 0.5$ cent; of 1 lb. nitric acid, specific gravity $1.48 = 7.5$ cents. But acid of 1.48 specific gravity contains only 88 per cent. of $H(NO_3)$, hence 1 lb. of HNO_3 costs $\dfrac{7.5 \times 100}{88}$

$= 8.52$ cents. Thus 1 lb. of $H_2(SO_4)$, if made by this reaction would cost in material alone

$$\left.\begin{array}{l} \text{for S } \dfrac{32 \times 0.5}{98} = 0.16 \text{ cent} \\[2mm] \text{for } H(NO_3) \dfrac{126 \times 8.5}{98} = 10.9 \text{ cents} \end{array}\right\} = 11.06 \text{ cents.}$$

Now, the 66° Bé. sulfuric acid which contains 93 per cent. H_2SO_4 is sold for 2.5 cents per lb. or nearly $\frac{1}{4}$ of the 11.06 cents. The oxygen of the niter is too expensive for our purpose. Supposing we change S into SO_2, by burning the sulfur in air, the oxygen of which costs nothing, and then conducting the SO_2 into the $H(NO_3)$, then we obtain

$$3SO^2 + 2H(NO^3) = H^2O + 3SO^3 + 2NO$$

and by adding water

$$3SO^2 + 2H(NO^3) + 2H^2O = 3H^2SO^4 + 2NO.$$
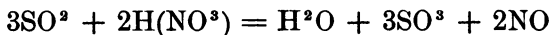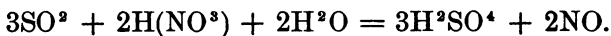
By this reaction the cost of materials will be cut down to $\frac{1}{3}$ or 3.66 cents. Even this is too much. But we have seen that the gas NO becomes NO^2 in presence of air, and that NO^2 reacts upon SO^2 thus

$$SO^2 + NO^2 = SO^3 + NO$$

or $SO^2 + H^2O + NO^2 = H^2(SO^4) + NO.$
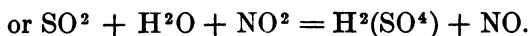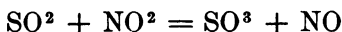
Deduction : The gas NO can be made the *carrier* of the atmospheric oxygen or even more pertinently the *transfer agent*. This reaction, then, points out the road for the *cheap* manufacture of $H^2(SO^4)$, for, theoretically we need only to buy the sulfur. The theoretical conditions would become realized in practice, if we could burn the sulfur in pure oxygen. But the latter requires $KClO^3$, and turns out more expensive even than the niter-oxygen. The chemical engineer is forced to make a compromise between what is best and what is cheapest. For, since 1 volume SO^2 contains 1 volume of oxygen we must admit for every volume of sulfur vapor, 5 volumes of air, hence follows the mixture of 5 volumes, one of which is SO^2 and four are N. In addition to this, 2.5 more volumes of air must be admitted to furnish the one-half volume required for the transfer by NO so that SO^3 may result. Thus 6 volumes of indifferent, or useless, nitrogen must be steadily removed from the vessel in which the transferring action takes place. This

cannot be done without at the same time re-
moving the NO (the transfer agent), while the
H^2SO^4 condenses to a liquid and thus removes
itself. The French chemist Gay-Lussac's ingenuity
intervened, however, and saved a very large per-
centage of NO; and thus made the low price of the
sulfuric acid possible, while yet leaving a margin
of profit in the manufacture. Another saving in
the cost came in with the substitution of *pyrite* for
sulfur. The mineral pyrite is FeS^2 and contains
$2 \times 32 = 64$ sulfur for every 56 of iron, or 1
pyrite $= 0.533$ of sulfur, a little more than $\frac{1}{2}$ its
weight. As some sulfur always remains with the
iron, we may say that pure pyrite yields 50 per
cent. of sulfur in form of SO^2 if properly handled.
The action occurs thus:

$$2FeS^2 + 11O = Fe^2O^3 + 4SO^2, \text{ (if complete.)}$$
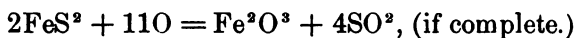
240 pyrite+176 oxygen=160 iron oxyd+256 sulfur
dioxyd. If burnt in air we have an addition of 4
vols. of $N = 616$ nitrogen. These numbers, of
course mean weight. 1 c.c. of SO^2 weighs 0.00285
gram hence

$$256 \text{ grams } SO^2 = \frac{256}{0.00285} = 89824 \text{ c.c.} = 89.8$$
$$\text{liters.}$$

1 c.c. of N weighs $= 0.001256$ gram, hence 616
grams

$$N = \frac{616}{0.001256} = 490.4 \text{ liters.}$$

For 1 liter of SO^2 we have about 5 liters of nitro-

gen.   But we must provide with this also the oxygen necessary to make SO^2 into SO^3. SO^2 contains $\frac{1}{2}$ volume S and one volume O, hence 1 volume SO^2 requires $\frac{1}{2}$ volume of O or $2\frac{1}{2}$ volumes of air, thus making a total of 1 volume $SO^2 + 5$ volumes of $N + 2\frac{1}{2}$ volumes of air = *8.5 volumes*, leaving the pyrite burners.   In this mixture of gases the volume percentage of SO^2 is *11.76*.   If this percentage falls below 4, the conversion becomes incomplete, as demonstrated by experience.   As was to be expected, experience showed the necessity of an excess of oxygen over that which the calculation demands. Hence the average composition of the gas mixture, in leaving the pyrite burner, is like this : N = 81 ; $SO^2 = 8.8$; O = 9.6 in 100 volumes.   The plant (equal to what in laboratory speech we call apparatus) for the manufacture of sulfuric acid comprises the following principal parts: 1, *the burners ;* 2, *the Glover tower ;* 3, *the lead chamber ;* 4, *the Gay–Lussac tower ;* 5, *the concentrating outfit.*   The diagram, Fig. 63, shows the arrangement of the plant in ground plan.   *BBB* are three burners or kilns for pyrite ; *D* is the dust chamber, of brickwork for the purification from solid particles of the gas ;   *G* is the Glover tower ; *MC* is the mixing lead-chamber and *C'* is the main lead-chamber ; *GL* is the Gay–Lussac tower with the chimney attachment *Ch*, from which the waste gases escape into the air.   In Fig. 64 the plant appears in sectional elevation.   The pyrite burner shows as a rectangular shaft or stack about 12 feet high and built of fire-brick.   Several of them

Fig. 63.
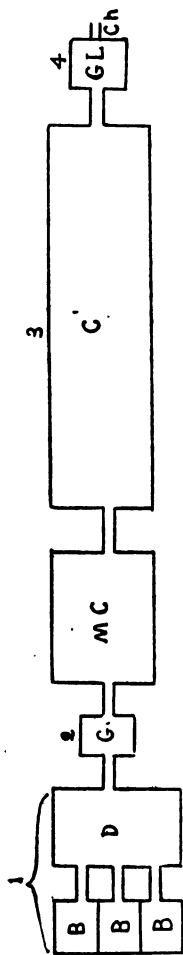
Fig. 64.
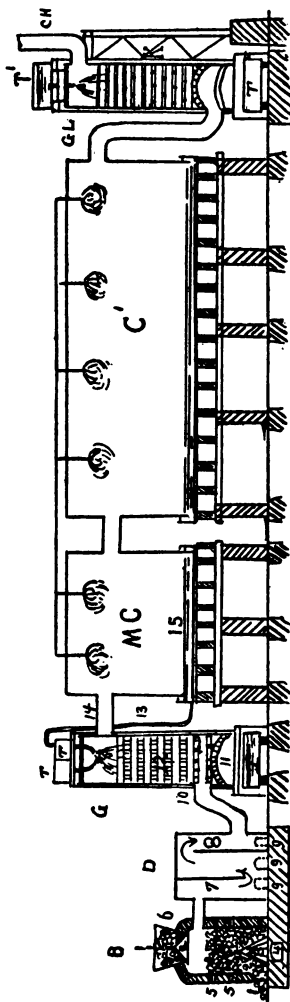
are generally built close together in a row (see ground plan).   Two opposite doors 1, 1 allow the iron oxyd to be drawn out, while a bell and hopper arrangement, 2, serves to introduce the pyrite, without losing any gas.   At 3 is a strong cast-iron grate in the form of a cone ; through the canal 4 air is admitted to this grate.   Small inlets 5, 5, 5 admit air to the upper part, when necessary.   The burner is started with a wood fire, until the lower furnace walls are at red heat.   Then small charges of pyrite are introduced until the stack is full to within 6 feet of the top.   The burning of the sulfur into SO^2 furnishes all of the heat needed from this period on.   A 1-foot iron pipe takes the gases from each burner into the dust chamber D which is built of common brick ; two vertical partitions 7, 8 divide the chamber into three sections and force the gases to a broken up and down course shown by the arrows.   Doors 9, 9 permit the removal of the ore-dust from time to time.   A two foot iron pipe, 10, takes the gases to the *Glover tower* G so named after its inventor.   It forms a brick stack of square section ; the inside is lined with hard glazed bricks which resist the action of the acids. A perforated arch of such bricks, 11, serves to support a structure of loose, hard, stoneware bricks and cylinders 12.   The idea is to present a very large surface over which the acid which comes from tank T above the tower, can spread and come in contact with the hot gases.

Purpose and function of the Glover tower.   (1) To cool down the gases to the temperature needed in

the chambers.   (2) To utilize the *nitrose* from the Gay–Lussac tower.   The term "nitrose" was introduced to designate the combination $H^2SO^4.NO$. The nitrose is pumped from the tank, *T*, under the Gay–Lussac tower, by means of air pressure through lead pipes into the one-half of the tank, *T*, on top of the Glover, and the *dilute* acid formed in the chamber, *MC*, is pumped through pipe line, *13*, into the other half of *T*.   From these tanks properly regulated streams pass through air-tight openings of the top of the tower upon the cylinder which forms the apex of the stoneware pyramid.   Here the concentrated nitrose in mixing with the dilute chamber acid sets free the *NO*, while the now semi-concentrated acid in running over the large brick surface comes to boiling in contact with the hot burner gases, splits into concentrated acid, which collects below the arch, and is drawn thence by automatic syphon in the tank, *T*, under the tower, whence it is pumped to the top of the Gay–Lussac tower to begin a new circuit of absorbing NO, etc., *ad infinitum*.   Aqueous vapor from the boiling acid in the meantime has mingled with the liberated NO, and with the other gases passes through pipe, *14*, into the mixing chamber, *MC*.   Here the action sets in :

$$SO^2 + O + NO + H^2O = H^2(SO^4) + NO.$$
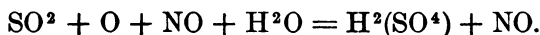
The H^2SO^4 + water vapor forms a dense white fog, which becomes liquid when it strikes a cool surface ; thus the principal precipitation occurs along the sides of the chamber, whence the acid runs down

into the leaden pan, *15*. Owing to the misty, foggy condition of the acid such an immense size of the chambers is required. From an average of fifteen English works, the chamber space is 21 cubic feet for *one pound* of sulfur burned in 24 hours. A plant, therefore, which is to produce five tons of 66° Bé. acid in 24 hours will require a chamber space

$$V = 10000 \times 0.94 \times 21 \times \tfrac{22}{68} = 64457 \text{ cubic feet.}$$

Making the chamber's cross section 20′ wide by 16′ high we get an area of 320 square feet, and hence $\tfrac{64457}{320} = 201.4$ feet. Such a length would be best broken into *3* chambers; to wit: A mixing chamber 50 feet long, a main chamber 101.4 feet long, an end chamber 50 feet long. The cost of the lead for these three chambers will be arrived at thus:

2 sides (201.4 × 16 each)	= 6445 square feet.
1 top 201.4 × 20	= 4028 square feet.
1 bottom 201.4 × 22	= 4430 square feet.
6 ends (20 × 16 each)	= 1920 square feet.
For Gay–Lussac tower and connection pipes	= 2000 square feet.
Total	18823 square feet.

Sheet-lead is rolled of many thicknesses, which are counted as so many pounds per square foot, hence 1 lb., 2 lbs., 3 lbs., . . . 12 lbs. sheet lead. Six lbs. per square foot is thick enough for the chambers, hence the total weight of lead will be 18823 × 6 = 112938 pounds, and at 6 cents per lb., this represents a cost of $6,776.28.

The Gay–Lussac tower and its functions. The purpose is to expose a maximum of surface covered with a moving film of concentrated H_2SO_4 to the ascending gas mixture from the last chamber. When thus exposed the H_2SO_4 will absorb NO. The absorption is proportional to the concentration
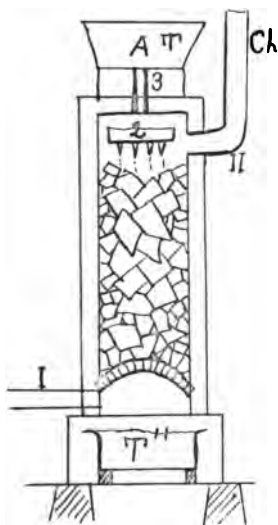
FIG. 65.   FIG. 66.
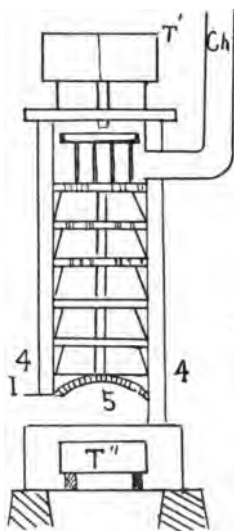
of the acid. Much aqueous vapor is in the gas mixture, which will be absorbed, and hence dilute the acid, lowering its capacity for NO. Thus comes the more recent practice of setting up two towers, one for drying the gases, the second for the absorption proper. *A,* Fig. 65, is a vertical section of the tower as commonly in use. Over a perforated arch

15

1 there lies a column of coke-pieces of fist size.
From a shallow tray *2*, studded with many small
dripping tubes falls the concentrated acid over the
coke, soaks into the latter and finally comes out as
nitrose through the arch *1* into a tank *T″* under
the tower.   The gases enter *I* and leave at *II* into
the chimney *Ch.*   A pipe *3* passes through the
leaden top (tightly) and feeds the acid from the
tank *T* into the tray *2*.

A more perfect arrangement is shown in Fig.
66, known as the Lunge-Rohrmann *plate column.*
The tower is of sheet-lead in wooden or iron frame.
Supporting ledges *4, 4* are provided, fused on (burned
on in technical speech) along the walls or sides.

FIG. 67.
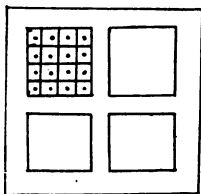
Similarly a central support *5* is provided of glazed
stoneware.   In the cross section Fig. 67, we see that
there are four plates, each one perforated by 16
holes, and each hole enclosed within a small square
area acting as a shallow reservoir.   It is claimed
for this system that it is quite superior in action to
the coke filling, inasmuch as the surface is very
large and yet regular, especially when the perfora-
tions of the alternate plates are not directly above

one another, but so that the liquid drops from the
upper hole upon the dividing ridge of the lower
panel.

Concentration of the chamber acid.   Experience
demands that enough water be delivered to the
chamber, as steam or as spray, so that the con-
densing acid corresponds about to the tri-hydrate
$H^2(SO^4).3H^2O$.   This liquid's specific gravity is
50° Bé. corresponding to 64 per cent. H^2SO^4.   For
many purposes such a strength is sufficient, for others
it must be made as strong as possible.   Between the

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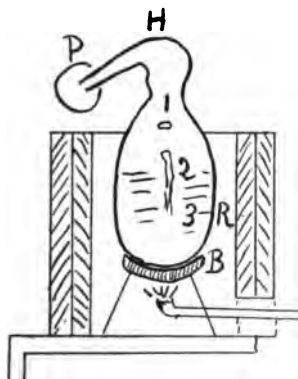
FIG. 68.   FIG. 69.

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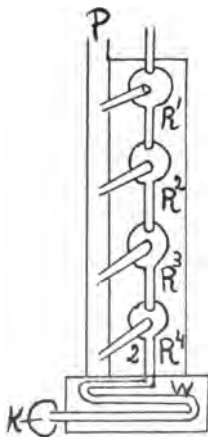
two extremes lies the strength of 60° Bé. $= 80$ per
cent. $H^2(SO)^4$.   This grade is known in the trade
as *pan acid*, because it is obtained by heating the
chamber acid in leaden *pans*.   At a higher concen-
tration than 60 per cent., the hot acid begins to at-

tack the lead of the pan, making white lead sulfate
and SO^2. The further concentration must be carried
on in retorts of either glass or platinum. Large
glass retorts break easily; those of platinum are
very costly. Hence a combination of the two is
sometimes used in which the bottom is of platinum,
the top or helmet of glass, or the helmet of lead.
Figs. 68 and 69 illustrate the Gridley system of con-
centrating in glass retorts by continuous process.
Fig. 68 shows one retort R in elevation, while Fig.
69 is a ground plan showing the combination of 4
retorts into a self-acting system. We see the retort set
into an iron basin with a layer of coarse sand between
iron and glass. Heat is applied to each retort sepa-
rately by a Bunsen burner of sufficient size. Each
retort has an inlet for the weak acid 1 and a syphon
outlet 2 (see ground plan specially). The helmet H
carries the weak-acid distillate into the pipe P of
sheet-lead. As each retort of a set stands higher
than its oneside neighbor and lower than the other
neighbor, the acid of steadily increasing strength
flows from R_1 to R_4 and from R_4 into the cooling
worm W, which lies in a stream of running water;
from the worm the acid of 65.5° Bé. flows into the
carboy K. By general agreement this is the cheapest
way of concentrating sulfuric acid. But only acid
of 92 to 93 per cent. can be made by it.

In Figs. 70 and 71 we see an all-platinum still of
the most modern construction, for making acid of
98 to 99 per cent. H^2SO^4, as furnished by the firm
of Lemaire and Co. of Paris. The strenuous effort

necessary is divided between two stills A, B, each
upon a separate fire-place F, F'.   Each still is a flat,
elliptical vessel, Fig. 71, ground plan.   The still is
in three detachable pieces, 1 the pan, 2 the lid, 3 the
helmet and snout to carry off the vapors.   (Snout
not shown.)   The older forms of still are circular.
The elongated form is chosen because it gives a
more economical use of the heat.   The pan 1 is dif-
ferent in the two stills.   In A the pan has 4 longi-
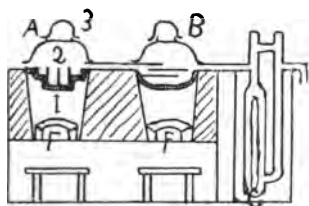
FIG. 70.   FIG. 71.
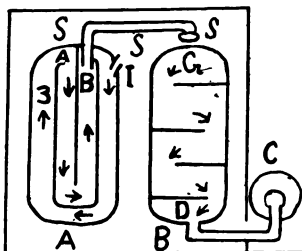
tudinal compartments, it consisting in fact of 2 con-
centric pans, the inner about ¾ inch deeper than the
outer.   Thus a larger surface of evaporation is
gained.   Now supposing the acid of 56° Bé. being
fed into A at the point I, it will flow along the
outer compartment as the arrows point.   The cur-
rent will pass through an opening in the partition
at a into the inner compartment and circulate to b,
whence the syphon tube S, S, S will draw it into the
still B at G.   The partitions in B are transverse and
do not touch the bottom, but leave ⅜ inch opening.
This is necessary for cleansing the pan as from the

highest concentrated acid a small percentage of iron sulfate precipitates. But here too a meandering of the current is brought about as the arrows indicate. At d another syphon tube takes the concentrated acid to the cooler C whence it goes either to the carboys or iron tanks, because at ordinary temperatures the strongest H_2SO_4 does not act upon iron. It is found that by the best care the platinum will dissolve in the strong acid at about the rate of 1 gram per ton of acid. For five tons daily production the bottom pan of the still will therefore lose $300 \times 5 = 1500$ grams a year and can at best last 2 years.

MANUFACTURE OF OIL OF VITRIOL AND SULPHURIC ACID BY THE CONTACT PRINCIPLE

1. *Oil of vitriol and SO_3 by Winkler's method.* Fundamental facts represented by the following equations:

(a) H_2SO_4 (93 per cent. acid) + contact surface at yellow heat = $H_2O + SO_2 + O$ + aq.

(b) $H_2O + SO_2 + O$ + aq. + cold contact surface = Water + ($SO_2 + O$), (moist gases).

(c) $SO_2 + O$ + moisture + spray of concentrated acid = $SO_2 + O$ + less conc. H_2SO_4 (dry gases).

(d) $SO_2 + O$ (dry) + platinated asbestos (at dull red heat) = SO_3 (as white vapor).

(e) Spray of H_2SO_4 (93 per cent. acid.) + nSO_3 = $H_2SO_4 + nSO_3$ = oil of vitriol,

In words: 93 per cent. acid is broken up into $H_2O + SO_2 + O$ by being spread over a highly heated surface of acid-resisting material. The resulting mixture of water vapor, sulfur dioxyd and oxygen is passed through cooling tubes in which most of the water vapor becomes liquid water. The gases are then sent over an extended surface of 93 per cent. acid (a fine spray) by which the water-vapor becomes fully absorbed, and lastly the mixture of dry $SO_2 + O$ is passed through a cylinder heated up to dull red heat, and filled with asbestus over which a film of platinum has been spread. Here then the platinum is the carrier for the oxygen, or the *transfer agent*, as in the ordinary process the *NO* is the transfer agent.

Finally the SO_3 can either be condensed in glass vessels as solid, silky, trioxyd, or it can be sent against a fine spray of 93 per cent. acid, in which the SO_3 dissolves. By increasing or decreasing the volume of the spray one will be able to get *oil of vitriol* (fuming sulfuric acid) of any degree of strength. Simple as the process appears, there are considerable technical difficulties, notably the difficulty of keeping the apparatus from rapid deterioration.

2. *Making sulfuric acid by contact directly from the pyrite.* The principle which underlies this plan is the same as in the preceeding. Why can we not make H_2SO_4 by passing the mixture of gases coming from the pyrite burner, namely nitrogen, sulfur dioxyd, and oxygen, directly over platinated as-

bestus? The question has been asked. At first sight there seems to be no valid objection and the experiment proves the feasibility. The cost should certainly be less, no lead chambers, no expensive stills required for the concentration. Works have been built on this plan and run for a number of years. It seems however that the conversion of SO^2 into SO^3 is incomplete owing to the presence of the large volume of nitrogen. Likewise the condensation of the SO^3 in this diluted condition is very difficult and gives much weak acid, which has to be concentrated after all. Thus the chamber method is not likely to become superseded for some time, or until the present difficulties of the contact method have been finally overcome by ingenuity and experience.

CHAPTER XIV.

OTHER COMPOUNDS OF SULFUR.

We may say that sulfur posesses a strong leaning or affinity towards combination with the metals nearly equal in this respect to oxygen and chlorine. The product of the union we call sulfid.

CuS	CuO	CuCl^2
Copper Sulfid	Copper Oxyd	Copper Chlorid.

Oxyds and sulfids are mostly insoluble in water; chlorids are mostly soluble in water. It follows that the so-called metallic ores are either sulfids or oxyds. Thus the iron ores are oxyds and sulfids: Fe^{2}O^3, Fe^{3}O^4; and FeS^2. The copper ores are Cu^{2}S, CuS, CuFeS^2, Cu^{2}O, CuO (exceptionally native copper, Cu). The lead ore is PbS, zinc ores are ZnS and ZnO. Tin ores are CuSnS^2 and SnO^2. The only exception among the common metals is aluminum; of it only the oxyd Al^{2}O^3 is known but no combination with sulfur, except in the form of a *sulfate*, Al^2(SO^4)^3. This means that aluminum has no affinity for sulfur at ordinary temperature and in water solutions. In a general way we conclude that nature utilizes the affinity between sulfur and the metals to concentrate the latter within the rocks and thus make it possible for man to mine and extract them at a profit. Example: Rub together with

mortar and pestle, 1, a drop of mercury and sulfur ; 2, finely divided metallic copper and sulfur.   In either case a new, black substance is formed, the sulfids of mercury and copper.   Gentle heat in a closed vessel converts the black sulfid of mercury into a dark-red sulfid of the same composition and when ground fine it is called *vermilion.*

The copper sulfid CuS has a blue color ; it corresponds to the natural mineral *covellite* or *indigo copper.*   Kept at a red heat in a glass tube, which is closed at one end, it changes into the bright grey sulfid Cu^2S thus :

$$2CuS + red\ heat = Cu^2S + S$$

one-half of the sulfur subliming into the cooler part of the tube.

Hydrogen sulfid (old name sulphuretted hydrogen).

FIG. 72.
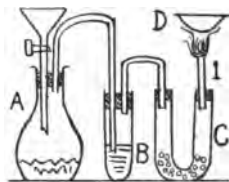
In acting with dilute H^2SO^4 or dilute HCl upon iron sulfid or zinc sulfid a very peculiar odor appears, due to a rapidly generating gas.   Let *A*, Fig. 72, be a flask holding about 250 c.c., fitted with stopper funnel tube and evolution tube.   Bring into it 20 grams of iron sulfid (FeS) and allow the acid to fall in drops from the funnel.   (5 % H^2SO^4 must

be used). B is the wash tube with water and C is a U-tube filled with $CaCl^2$ in small pea size.   The gas will issue dry and pure at the narrow opening *1*.   If a match be applied the gas will burn with a pale blue flame and if a dish D with clean undressed face and containing cold water be held into the flame, drops of colorless liquid (water) and yellow sulfur will be precipitated upon the dish D, whilst the pungent odor of SO^2 is given off.   Hence the gas must be composed of S and H.

Proof that the compound is H^2S.   Let the gas enter the knee-tube, (Fig. 73), over mercury, until the latter's level is below the knee ; mark the level with

FIG. 73.
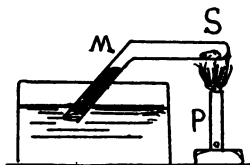
sticker, M.   Introduce a piece of tin, S, and shove it to near the end of the knee-tube.   Bring S to red heat with lamp.   Tin unites with the sulfur, forming brown SnS.   After cooling we find volume of gas unchanged.   We reason since 1 volume H^nS^m con-tains 1 volume H, then

Weight of 1 volume H^nS^m = 1.521
Deduct wt. of 1 vol. H   = .089
                       ————
                       1,432 = weight of S.

But 1.432 is equal to the wt. of $\frac{1}{2}$ vol. sulfur, hence one vol. H^nS^m contains 1 vol. of $H + \frac{1}{2}$ vol. S, or 2 vols. of $H + 1$ vol. S—the symbol is H^2S.   100 grams of H^2S contain $S = 94.2$; $H = 5.8$ grams. Now we can write the equation of formation :

$$FeS + H^2SO^4 = FeSO^4 + H^2S$$

$$FeS + 2HCl = FeCl^2 + H^2S.$$
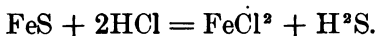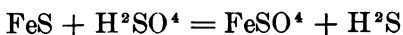
Generation of H^2S in a steady current at the minimum of cost. This is a very important problem, because in all analyses, both qualitative and quantitative, H^2S must be used. Different forms of apparatus have been described by inventors. Of all those the Koenig's apparatus serves the purpose best. It has already been described on pp. 61 to 63, Fig. 28, for the generation of chlorine gas in a steady, long-continued current. The apparatus is universal, may be used whenever a gas is to be produced from a solid by means of a liquid acid. Read over the description on pages 61 to 63, with the following changes : The generating tube, *G*, is to be charged with pieces of iron sulfid, FeS, of hazel-nut to pea size, the funnel being removed, up to the end of the funnel tube. (For chlorine we only fill the tube one-third.) The funnel bulb contains 5 per cent. H^2SO^4 (never any stronger), 27 c.c. of concentrated H^2SO^4 in 1000 c.c. of water. This dilute acid acts upon FeS at ordinary temperature, but more energetically at 60° C., to which temperature the small flame at *b* heats the water in the jacket, *J*.   Regulate the stop-cock at *F* so that a drop

of acid will issue per second. The gas will then
flow from the goose-neck, L, in a strong, even cur-
rent.   The other product, which is a water solution
of $FeSO^4$ with a small quantity of free acid, will be
discharged through the rubber tube, R, into the flask,
W. Thus the acid from above will act upon a
material surface always clean, always under equal
conditions, and hence produce the same quantity of
gas per minute.

Note. The pressure of the gas is equal to a col-
umn of water of the length of the funnel tube,
provided that the length of the tube, R, from its
lowest point in the bend to the discharge at P be
equal to the length of the funnel tube or greater.
If you should connect the rubber from the goose-
neck to a long tube and dip the latter to the bottom
of a high beaker-glass filled with water, so that the
length of the water column be greater than the
length of the funnel tube, then the gas will not go
through the liquid, as it should do, but it will
escape through the funnel or at P.   The funnel can
be supplied from a large bottle by means of a syphon
and a pinch-cock or a glass stop-cock.   The funnel
holds sufficient acid for any ordinary operation in
analysis.   One often neglects to look after things at
the right time, and so in this case the whole charge
of iron sulfid might be used up by sheer neglect if
the acid supply kept on running.

Properties of H^2S.   Strong, unpleasant odor.
Colorless. At 11° C. under a pressure of 15 atmos-
pheres, $15 \times 15 = 225$ lbs. per square inch, the gas

becomes a mobile, colorless liquid. The latter becomes a white, snow-like mass of crystals at $-85°$ C. The gas acts as a poison on man and animals, producing faintness, headache; if persistently breathed it causes death. A horse was placed in a large room which had been made thoroughly air-tight. One-half per cent. by volume of H_2S was mixed with the air of the room, then closed. The horse died in 15 minutes. Always generate the gas under a well-drawing hood or in the open air. One volume H_2S weighs 1.180 if the same volume of air weighs 1.000. By calculation the specific gravity is 1.1747 when air $= 1$, and 18 for $H = 1$. One c.c. of air weighs 0.001293 gram, therefore 1 c.c. H_2S will weigh $0.001293 \times 1.180 = 0.001526$ at $0°$ C. and 760 mm. mercury pressure.

One volume water at $15°$ C. absorbs nearly three volumes H_2S. The resulting solution contains $0.001526 \times 3 \times 100 = 0.4578$ p. c. of H_2S by weight, about *0.5 per cent.*, and is named *H_2S water*. The solution does not keep. It decomposes rapidly in the sunlight, thus H_2S + water $+ O +$ sunlight $= S + H_2O +$ water. It will keep longer if the water has been boiled, then cooled quickly, before passing the H_2S into it, and if the bottle is then sealed air-tight before the oxygen of the air can dissolve again in the water. Brown-glass bottles are best, because the active sun rays do not penetrate much through such glass. H_2S water freshly prepared is a very handy reagent both in qualitative and quantitative work. The H_2S water shows *slight*

acid action on litmus. The gas itself decomposes more readily than H^2O, thus:

H^2S in red-hot glass tube $= H^2 + S$ (sulfur deposits).

$H^2S + H^2SO^4 = H^2 + S$ (sulfur floats on the acid).

H^2S + electric spark $= H^2 + S$ (Put 10 c.c. of gas into eudiometer over mercury and let the spark pass over; sulfur deposits as a snowy cloud and 10 c.c. of hydrogen are left. This is another proof of its composition of 1 vol. H $+ \frac{1}{2}$ vol. S.)

Because concentrated H^2SO^4 decomposes the gas, we reason that one must not use H^2SO^4 as a *dryer*, but $CaCl^2$ instead, for this gas.

ACTION OF H^2S UPON THE ALKALINE HYDROXYDS.

The gas is eagerly absorbed by both weak and strong solutions of KOH, NaOH, NH^4OH.

(a) *Action of H^2S upon $K(OH)$ in water at air temperature.*

$H^2S + K(OH) = K(SH) + H^2O$ and $H^2S + 2K(OH) = K^2S + 2H^2O$. Dissolve about 5 grams of KOH in 25 c.c. of water. Divide the liquid into 2 equal parts in two test-tubes. Let H^2S pass into one of the tubes until there is no further absorption, that is, until the size of the bubbles does not diminish in the ascent through the liquid, and you smell the H^2S strongly. Then the colorless liquid will contain $K(SH)$, potassium sulfohydroxyd. Now pour the contents of the other tube into the first and you will have

$$K(HS) + KHO = K^2S + H^2O.$$
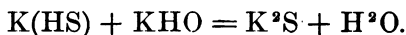
The solution of potassium sulfid is likewise a colorless liquid. The properties of the two bodies are not quite alike. Both, by gentle evaporation over H^2SO^4 in a dessicator (a glass vessel with a ground rim and ground cover or plate of glass), give crystals, but they do not belong to the same system.

K(SH) can stand red heat without decomposition if made in the following way in a glass retort, no water being present:

$$K^2CO^3 + 2H^2S + red\ heat = 2K(SH) + CO^2 + H^2O.$$
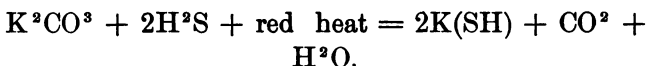
In this respect it acts like the hydroxyd K(OH). It is a *sulfo base*, which can form with *sulfo acids*, *sulfo salts*.

(b) *Action of H^2S upon Na(HO).*

$$H^2S + Na(OH) + water = Na(SH) + H^2O.$$
$$H^2S + 2Na(OH) + water = Na^2S + 2H^2O + water.$$

They act like the potassium compounds.

(c) *Action of H^2S upon $NH^4(HO)$.*

$$H^2S + NH^4(HO) = NH^4(SH) + H^2O.$$
$$H^2S + 2NH^4(HO) = (NH^4)^2S + 2H^2O.$$
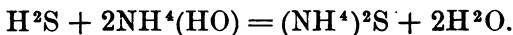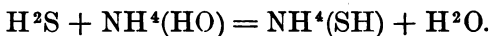
Both colorless solutions.

(d) *Action of H^2S upon $Ca(HO)^2$.*

Make 2 grams of quicklime into milk of lime with 20 c.c. of water and pass H^2S into solution until saturated; the solution becomes clear in measure as the hydroxyd passes into the sulfohydrate, thus

$$Ca(HO)^2 + 2H^2S = Ca(SH)^2 + H^2O.$$
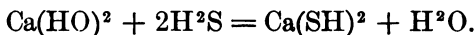
The solution of the sulfohydrate decomposes during evaporation, into CaS and H^2S; the *CaS is not soluble in water.*

$Ca(SH)^2$ is used by tanners to remove the hair from the hides. Even from the living skin the hair falls out when the solution is repeatedly applied.

Calcium monosulfid, CaS, is best prepared in the dry way. Mix gypsum with charcoal powder in the proportion of gypsum 3.6 parts, charcoal 1 part, and heat the mixture in a fireclay crucible to full redness in a suitable furnace until the blue flame stops burning at the small opening left in the lid of the crucible.

$$CaSO^4.2H^2O + 4C + \text{red heat} = CaS + 2H^2O + 4CO.$$
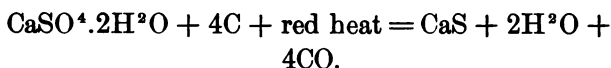
The porous mass of CaS is white, when the materials are pure. It is mostly somewhat reddish-yellow. If exposed to the sunlight during the day it will be luminous during the dark of the night. It is a *phosphorescent body.* It is used for faking ghosts. When mixed with water it decomposes:

$$2CaS + 2H^2O = Ca(SH)^2 + Ca(HO)^2$$

The solutions of the alkaline sulfids become yellow after some time of standing in contact with the air. This phenomenon is due to the forming of *polysulfid* thus:

$$2K^2S + H^2O + O = 2K(OH) + K^2S^2, \text{ pot. disulfid.}$$

$$2K^2S^2 + H^2O + O = 2K(OH) + K^2S^4$$

$$2K^2S^n + H^2O + O = 2K(OH) + K^2S^{2n},$$
$$\text{pot. polysulfid.}$$

16
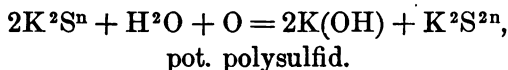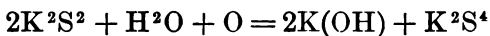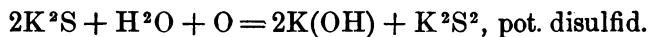
As the action advances the color of the liquid deepens until it becomes blood-red; the capacity of the potassium for sulfur is now satisfied, $(2n = 9)$ but the oxydation keeps on, the solution deposits sulfur in crystals, the color becomes lighter until, at last, a cloudy solution remains with the sulfur all separated out in crystals; the liquid is $K(OH)$ water thus:

$$2K^2S^9 + H^2O + O = K^2S^8 + 2K(OH) + 10S.$$
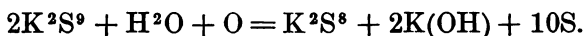
Oxydation, therefore, means substitution of O in the place of S. *Note.*—Write out these reactions for Na^2S and $(NH^4)^2S$.

ACTION OF SULFUR ON THE ALKALINE HYDROXYDS.

Bring flour of sulfur together with a strong solution of KOH $(1 : 3)$ into a test-tube. At ordinary temperature the action is too slow to be perceptible. On heating, the liquid assumes a yellow color, which grows in intensity at the boiling heat, while the sulfur disappears. No gas is seen to escape, hence the oxygen of the KOH, as well as the hydrogen, must enter into the new unions. The brown-red liquid acts upon copper or silver like $K^2S + H^2O$, that is to say, a black sulfid CuS or Ag^2S forms, while K^2 unites with the H^2O as $2KHO$. Hence we may assume that the first action of $2KHO$ upon S gives $K^2S + H^2O^2$. But the latter H^2O^2 is hydrogen peroxyd, a powerful oxydizing agent, which tends to transfer one O to any oxydizable body in its neighborhood, and this is S. Now we know two oxyds of sulfur, SO^2 and SO^3, either of

which might form, but in fact quite another combination results, namely, S^2O^2, and this oxyd combines thus with $2KHO$ to form $K^2(S^2O^3)$. Evidently one can explain this in another way by assuming first the forming of SO^2, then of $K^2(SO^3)$, and then the entering of one S into this molecule in presence of an excess of KHO and of S molecules. The final reaction presents itself in the balanced equation :

$$mKHO + nS + water + heat = 2K^2S^9 + K^2(S^2O^3) + 3H^2O + water + (m—6)KHO + (n—20)S.$$
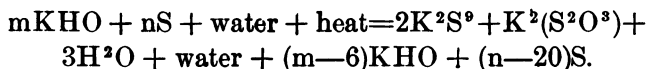
K^2S^9 is potassium polysulfid (the maximum of saturation), $K^2(S^2O^3)$ is *potassium thiosulfate* or *potassium hyposulfite*.

If NaHO be taken instead of KHO the action will be

$$6NaHO + 20S = 2Na^2S^9 + Na^2(S^2O^3) + 3H^2O$$
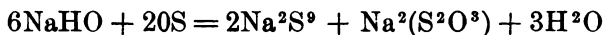
$Na^2(S^2O^3) + 10H^2O$ easily crystallizes in large, transparent, colorless crystals. It is the so-called *hypo* of the photographers because its water solution dissolves the insoluble AgBr of the negative plate, but not the metallic silver which resulted from the action of the developing agent upon the exposed plate, and therefore *fixes* the image. $Na^2S^2O^3$ also dissolves the insoluble $Pb(SO^4)$. It is the chief ingredient of the extracting solution in the *Russell process* for extracting the silver from its ores ; hence a most important substance.

Technical manufacture of the salt. Boil together NaHO, S and water until the sulfur is all dissolved.

Then pass SO^2 gas into the liquid until the yellow color has disappeared and allow the hot liquid to cool. The hyposulfite crystallizes. The proportions are: Solid NaHO 96 parts, flowers of sulfur 64 parts, water 500 parts. The principle of the action is that SO^2 takes from the polysulfid one S, turning into S^2O^2, and the latter decomposes 2NaHO to form $Na^2S^2O^3 + H^2O$. Thus:

$Na^2S^9 + 18NaOH + 9SO^2 = 9Na^2S^2O^3 + 9H^2O + Na^2S$, $H^2O + Na^2S + SO^2 = Na^2(SO^3) + H^2S$; $2H^2S + SO^2 = S^3 + 2H^2O$.
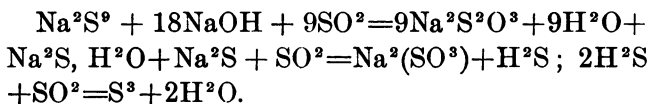
Ultimately there must be a precipitation of sulfur if an excess of SO^2 is run into the solution.

Second process. The raw material is here the waste product from the Leblanc soda process, which is essentially a mixture of $CaS + CaO$. If this waste be exposed to the action of air for a proper period an oxydation will set in, by which calcium thiosulfate, calcium sulfate and sulfur are produced. If this oxydized material be extracted with water the solution contains chiefly, $Ca(S^2O^3)$, calcium thiosulfate. On the addition of Na^2CO^3 we obtain a precipitate of $CaCO^3$ and a liquid holding $Na^2(S^2O^3)$. Evaporation and crystallization furnish commercial *hypo.*

Note. The oxyd SO or S^2O^2 has not yet been obtained in the free state. For as soon as an acid is added to a solution of hypo there is an action thus: $Na^2(S^2O^3) + water + 2HCl = 2NaCl + SO^2 + S$. This precipitation of sulfur, upon acidification, is an excellent means for recognizing the presence of a thiosulfate.

ACTION OF H^2S UPON THE SOLUTIONS OF METALLIC SALTS.

(1) Upon solutions of potassium, sodium, ammonium and calcium salts. We find that no action takes place.

$$K^2SO^4 + water + H^2S = K^2SO^4 + water + H^2S$$
$$Na^2SO^4 + water + H^2S = Na^2SO^4 + water + H^2S$$
$$(NH^4)^2SO^4 + water + H^2S = (NH^4)^2SO^4 + water + H^2S$$
$$CaSO^4 + water + H^2S = CaSO^4 + water + H^2S.$$
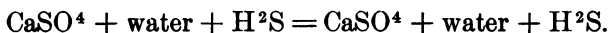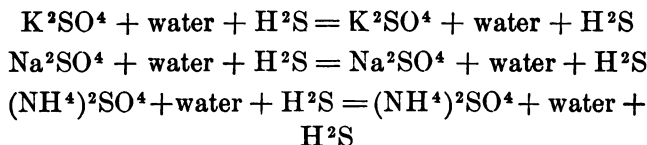
Reasons: If there were action it would have to be thus

$$K^2SO^4 + water + H^2S = K^2S + H^2SO^4 + water.$$
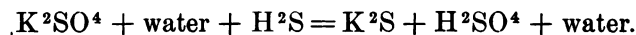
But we have seen that: $K^2S + water + H^2SO^4 = K^2SO^4 + water + H^2S$, and similarly for other sulfids; therefore the end equaling the beginning, there can be no action.

(2) Upon solutions of iron-zinc-aluminum salts.

$$FeSO^4 + water + H^2S = FeSO^4 + water + H^2S$$
$$FeCl^2 + water + H^2S = FeCl^2 + water + H^2S$$
$$Al^2(SO^4)^3 + water + H^2S = Al^2(SO^4)^3 + water + H^2S.$$
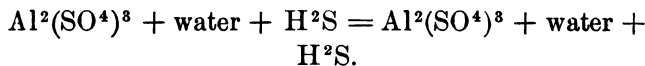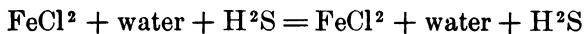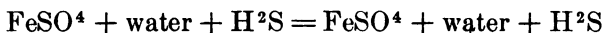
There is no action for the same reason as given above. We generate H^2S by acting upon FeS with very dilute H^2SO^4, hence H^2S cannot form FeS in presence of free acid, which must be formed simultaneously with the FeS:

$$FeSO^4 + water + H^2S = FeS + water + H^2SO^4.$$
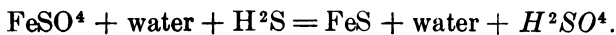
The same is to be said of zinc. But aluminum does not combine with the sulfur in H_2S under any circumstance, in water solution.

(*3*) *Action of water solution of* $K_2S, Na_2S, (NH_4)_2S$ *upon the solutions of iron, zinc and aluminum salts.*

There is always a precipitate formed, but this is not the same thing for all the three metals ; thus :

$FeSO_4 + water + K_2S = FeS + K_2SO_4 + water$
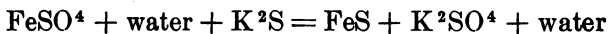
FeS forms as a voluminous *black* precipitate. Why ? Because there is no H_2SO_4 formed, but K_2SO_4, and K is the most positive of the metals, most difficult to be displaced in its salts.

$Na_2S,(NH_4)_2S$ act the same. Write the equations.

$ZnSO_4 + K_2S + water = ZnS + K_2SO_4 + water$
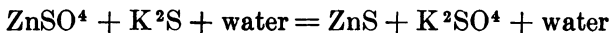
ZnS is a *white* flocculent precipitate. Reason as before.

Write equations for $ZnSO_4 + Na_2S, (NH_4)_2S$.

$$Al_2(SO_4)_3 + 3K_2S + water = 2Al(OH)_3 + 3K_2SO_4 + 3H_2S$$
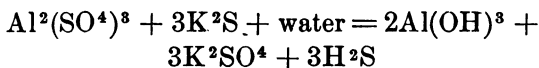
as there is no affinity between Al and S, the latter must form H_2S. Aluminum hydroxyd forms instead of the sulfid.

(*4*) *Action of* H_2S *upon the solutions of lead, copper, tin, mercury, silver and gold salts.* Here we find that precipitation of the sulfids occurs whether the solutions be neutral or whether they contain free acid.

PbS, a flocculent, *brownish-black* precipitate from cold solutions, a *bluish-grey* from a hot solution.

CuS, a flocculent *brownish-black* precipitate.

SnS, a flocculent *brown* precipitate from *stannous* salts.

SnS², a flocculent *yellow* precipitate from *stannic* salts.

Ag²S, a flocculent *black* precipitate.

Hg²S, a flocculent *brown-black* precipitate.

Au²S³, a fine, granular, *brown* precipitate.

$$8AuCl^3 + 3H^2S + 12H^2O + heat = 8Au + 24HCl + 3H^2SO^4.$$
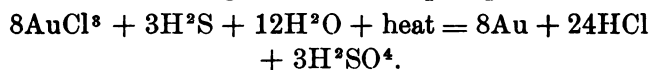
This means that the gold sulfid has very slight stability, heat causing the *metal* to precipitate. The marked difference in the action of the metal solutions towards H²S will suggest at once the utilization for separating a mixture of salts by means of H²S. Let a solution be made up containing the following chlorids: SnCl⁴, CuCl², HgCl², AlCl³, FeCl², ZnCl², CaCl², NaCl and KCl. Let HCl be added and then H²S passed through it, the liquid being warm, but not boiling. A precipitate falls, being a mixture of *SnS²*, *CuS*, *HgS*. When the liquid smells strongly of H²S filter and call the precipitate of mixed sulfids (*A*). The filtrate is then made alkaline with NH⁴OH, and another precipitate falls, of what? Of *Al(OH)³*, *FeS*, *ZnS*. Why? Because the filtrate contains H²S in solution which becomes (NH⁴)²S when NH⁴HO is added, and the (NH⁴)² acts upon the Al, Fe, Zn salts as soon as the free HCl is neutralized by (NH⁴)HO. Pass H²S into the liquid in order to make a *complete* precipitation, until liquid smells strongly of ammonium sulfid.

Filter and call this precipitate (B). Into the filtrate pass CO_2 gas. Why? Because we know that calcium carbonate is insoluble in water, and this solution being alkaline with ammonia, the CO_2 will form $(NH_4)_2CO_3$ and this will give with $CaCl_2$, $CaCO_3$ plus $(NH_4)Cl$. Filter. Name this precipitate (C). In filtrate can now be only $KCl + NaCl + NH_4Cl + (NH_4)_2CO_3 + (NH_4)_2S$. Evaporate to dryness in porcelain dish, then heat over direct flame until the ammonium salts have smoked away. Dissolve the residue (KCl, $NaCl$) in 1 or 2 c.c. of water. We have not come across an action by which we can well separate the 2 alkali metals from one another except the difference in the solubility of the sulfates and the nitrates. Convert $KCl + NaCl$ into $K_2SO_4 + Na_2SO_4$. How? By adding a few drops of H_2SO_4 to the 1 or 2 c.c. of liquid; by evaporating this liquid to dryness and by then heating to red heat until no odor of H_2SO_4 comes off. Because we know by experience the following actions:

$$2NaCl + H_2SO_4 + heat = Na_2SO_4 + 3HCl.$$
$$2KCl + H_2SO_4 + heat = K_2SO_4 + 2HCl.$$

Dissolve the residue in little boiling water; bring a drop upon a piece of glass, let evaporate and examine under the microscope. As the K_2SO_4 is very much less soluble than the Na_2SO_4, the former will crystallize first from the margin of the drops inward. In the center will be found the long prismatic crystals of Na_2SO_4, outside the stumpy, almost cubic crystals of K_2SO_4.

If the nitrate test is to be made the first steps must be the conversion of KCl, NaCl into KNO^3, $NaNO^3$. We remember that AgCl is insoluble in water and dilute acids, also that metallic silver dissolves in HNO^3 of medium concentration forming $AgNO^3$. If therefore we add the $AgNO^3$ solution to the KCl, NaCl solutions so long as the white cloud is forming, while stirring, then a change will occur thus,

$$KCl + AgNO^3 + water = AgCl + KNO^3.$$

Filtering off AgCl, a drop of the filtrate evaporated upon a glass slide will give the characteristic crystals of the two niters if both metals (K, Na) are present in the unknown substance, or the crystals of either alone, as the case may be. Since K salts impart to the mantle of the gas flame a *purple* color, and Na salts an *orange-yellow color*, properly applied flame test may decide the question of the presence or absence of either of the two metals, but it is not here the place to treat of these phenomena in greater detail.

Let us now turn our attention to the *precipitate* (*A*), and see how far our knowledge will enable us to separate and recognize the metals which it does, or may contain.

(*a*) *HgS.* All salts of mercury are volatile either as a whole, or at least the metal itself. If the mixture of sulfids includes HgS, we must get a sublimate of some kind by heating this mixture in a hard-glass tube, closed at one end. Three inches of the tube will suffice. (Precipitate must be dried

before placing it in the tube). Heat closed end to full redness : The sulfids melt, HgS sublimes. When tube has cooled, break off the closed end, crush glass and sulfids, act upon with HNO^3, pick out the glass and evaporate to dryness, then add water.

(b) If copper is present, a blue solution results, if tin, a white, pulverulent body of SnO^2; if lead, a white powder of $PbSO^4$. (Why? Because $3PbS + 8HNO^3 = 3PbSO^4 + 4H^2O + 8NO$.)

Filter and wash the filter with water. Squirt the white powder into a small beaker-glass and add a few grams of $Na^2(S^2O^3)$ sodium thiosulfate. (Hunt up this body under the action of S upon KOH, NaOH and study its formation.) Stir well 5 to 10 minutes, filter. $Na^2S^2O^3$ acts upon $PbSO^4$ thus :

$$PbSO^4 + 2Na^2S^2O^3 + water = Pb(S^2O^3).Na^2S^2O^3 + Na^2SO^4.$$
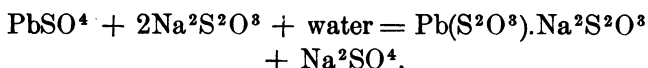
Lead-sodium thiosulphate is soluble in water, hence if you filter, the filtrate will contain the lead salt, and if a white residue be left on the filter it must be SnO^2. Boil the filtrate and blue-grey PbS falls out :

$$PbS^2O^3.Na^2S^2O + H^2O + heat = PbS + Na^2SO^4 + H^2O + SO^2 + S.$$
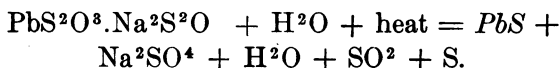
(c) Mix the filter ashes with the problematic SnO^2 together with a little Na^2CO^3. Press mixture into a cavity on a piece of charcoal, apply a good reducing flame with a blow-pipe ; break out the fused mass with a knife-point, grind up in a small mortar with water. If white flakes with metallic lustre show

themselves after washing away the charcoal, then the white powder was surely tin. We have thus proved the metals in precipitate (A) with no other means but such as our progressively acquired knowledge has furnished us.

Precipitate (B). We have present, presumably, FeS, ZnS, Al(OH)^3. It was found that all three dissolve in HCl:

$$FeS + 2HCl = FeCl^2 + H^2S.$$

$$ZnS + 2HCl = ZnCl^2 + H^2S.$$

$$Al(OH)^3 + 3HCl = AlCl^3 + 3H^2O.$$
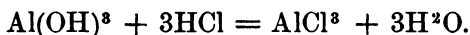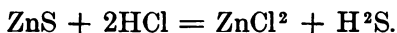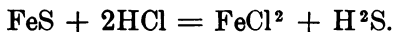
By boiling solution with 1 c.c. HNO^3, we shall convert FeCl^2 into FeCl^3, thus:

$$3FeCl^2 + 3HCl + HNO^3 = 3FeCl^3 + 2H^2O +$$
NO, the solution turns yellow. NH^4(HO) decomposes FeCl^3, AlCl^3, thus:

$$FeCl^3 + 3NH^4(HO) = Fe(HO)^3 + 3NH^4Cl.$$

$$AlCl^3 + 3NH^4(HO) = Al(HO)^3 + 3NH^4Cl.$$
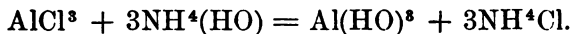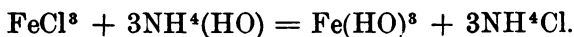
Fe(HO)^3, a *flocculent, brown* substance, insoluble in water and NH^{4}HO. But ZnCl^2 behaves differently towards NH^{4}HO; it gives first a *white flocculent* precipitate, but on adding more NH^{4}HO the precipitate dissolves.

$$ZnCl^2 + 2NH^4HO = Zn(HO)^2 + 2NH^4Cl.$$
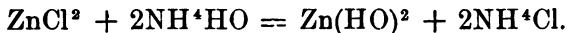
$$Zn(HO)^2 + 2NH^4HO = Zn(NH^4O)^2 + 2H^2O,$$
soluble in water and NH^4(HO). Hence it follows that we can separate Zn from Fe + Al by means of NH^{4}HO. Add NH^{4}HO to the hot liquid and stir until it smells strongly of NH^{4}HO; then, filter.

Into filtrate pass H^2S and white ZnS falls. Why? Make answer yourself from what was given above. The forming of a white precipitate proves the presence of zinc. Wash the precipitate from NH^4HO from filter into a beaker glass or porcelain dish, add $Na(HO)$, a couple of grams, and boil. $Fe(HO)^3$ is insoluble in $Na(HO)$; $Al(HO)^3$ is soluble in $Na(HO)$, because it combines with the latter to make soluble sodium aluminate.

$$Al(HO)^3 + 3Na(HO) = AlNa^3O^3 + 3H^2O$$
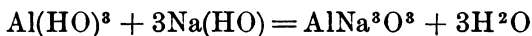
Filter. To prove Al in the filtrate, acidify with HCl and then add NH^4HO. If a white, flocculent precipitate falls, aluminum is present. Thus:

$$Al(NaO)^3 + 3HCl = AlCl^3 + 3NaCl \text{ both soluble.}$$
$$AlCl^3 + 3NH^4HO = Al(HO)^3(\text{insoluble}) + 3NH^4Cl.$$
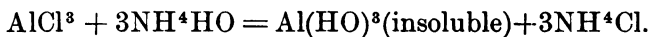
To prove that the brown substance is iron hydroxyd, dry it on a filter. Put some of the dry mass in a cavity on charcoal and heat in a reducing (yellow) flame with blowpipe; then test the mass with a magnet. If the substance clings to magnet the presence of iron is proved. Why? Because by the reducing flame the trioxyd Fe^2O^3 is changed either to *metallic iron,* or to the *tetroxyd Fe^3O^4* and *both* are magnetic. Thus:

$$Fe^2O^3 + 3C + \text{red heat} = Fe^2 + 3CO$$
$$3Fe^2O^3 + C + \text{red heat} = 2Fe^3O^4 + CO$$
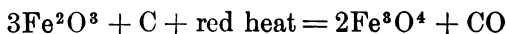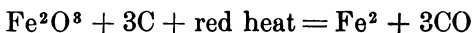
Precipitate (C). The white substance thrown down by $(NH^4)^2CO^3$ can only be $CaCO^3$ according to our present state of knowledge. Later on we will learn of several more elements whose carbonates

will fall with the calcium. But to prove the substance absolutely, ignite it with the soda at yellow heat. Then moisten with 1 or 2 drops of water. If calcium oxyd, it will slake, *i. e.* get warm and swell up a little. If it does, add a few drops of very dilute H_2SO_4 and heat, it will all dissolve; then allow one drop of liquid to evaporate on a glass slide, and examine the crystals under a microscope. They will be the characteristic needle-shaped or arrow-head shaped twins of $CaSO_4$.

Thus our analysis is finished. It was introduced at this point to show you that analytical chemistry simply means the thinking application of the chemical knowledge which we gradually accumulate by experiment.

SOME OTHER SULFUR COMPOUNDS.

Hydrogen persulfid, H_2S_2. Whenever you acidify a solution of ammonium, sodium, or potassium sulfid and then boil the solution, there will be at first only the odor of H_2S. But in measure as this odor becomes less pronounced, there will appear another odor, pungent and offensive, somewhat resembling the odor of fresh onions. As the eyes begin to smart if you peel and cut up an onion, so will the eyes become affected if exposed to the fumes arising from the above boiling solution. This odor is due to H_2S_2. This latter body is at ordinary temperature a yellow liquid, little soluble in water, and therefore separating from water in small oily drops. Preparation: Pour yellow Na_2S or $(NH_4)_2S$ into an

excess of dilute HCl or H_2SO_4 and let the milky liquid stand for some hours. Then pour off the liquid and you will find this yellow, evil-smelling substance at the bottom. There is no technical use for it at present.

Sulfur and chlorine, SCl. Place flowers of sulfur (2 grams) in a small tubulated retort and conduct dry chlorine gas into the retort. The chlorine is eagerly absorbed, generating heat, which must be removed by cold water on the outside. A red liquid forms. When the sulfur has all disappeared, close the tubulus of the retort and let the neck of the retort project into a receiver, cooled by hydrant water. Then heat the retort. A yellow-red liquid condenses in the receiver and finally sulfur remains in the retort. The original liquid was therefore a solution of sulfur in sulfur chlorid. The latter has specific gravity of 1.68. It fumes at the air because the air-moisture decomposes it:

$$4SCl + 2H_2O = 4HCl + 3S + SO_2.$$

The one property which makes this sulfur chlorid technically valuable is its solvent power for sulfur. 100 SCl dissolve 73 S. If soft india rubber is placed in this solution of sulfur in SCl, the rubber will absorb sulfur and become *vulcanized.* There are other combinations of S + Cl and S + Cl + O, but of no practical interest.

Sulfur and carbon, CS_2. Vapors of sulfur combine with carbon at a red heat forming a vaporous compound CS_2, *carbon disulfid.* On a large scale the substance is made in vertical retorts of cast-iron

lined with fire clay. The retorts are filled with small bits of charcoal and stand walled in so that they may be brought to red heat. The sulfur is introduced through an inclined tube at the bottom of the retort. The vapors of CS^2 are condensed against cold water. CS^2 sinks to bottom of condenser and can be drawn off. The first or raw product is far from pure and has a most offensive odor. By redistillation and shaking with metal chips as lead, copper or mercury, a colorless liquid is obtained whose odor is rather agreeable. In 1840 one pound of CS^2 was worth \$5.00; in 1860 only 5 cents; to such an extent had the process been improved.

Properties. CS^2 is a very mobile liquid. Sp. G. $= 1.268$. Boils at 46° C. High index of refraction. Very inflammable, burns with bluish-white flame. When a current of air blows through the liquid CS^2, soon snowy crystals form on the glass ($CS^2.H^2O$); the temperature falls to −18° C.; water dropped on the liquid freezes instantly. CS^2 easily dissolves animal and vegetable fats and oils, and it dissolves sulfur. Upon these facts are based the technical applications of carbon disulfid. (1). To extract the sulfur from the sulfur earth, where the latter is abundant (near active or near extinct volcanoes). (2). To extract the fat from bones (glue factories, stock-yard slaughter-houses). (3). To extract the oil from the seeds (cotton, flax, rape, poppy, olive, nut) more thoroughly than can be done by mere pressing of the crushed seeds. (4). To remove fat from raw wool; from woolen cloth

after dyeing with certain colors. In all of these processes much care must be exercised on account of the inflammability and the poisonous effects of the carbon disulfid. It produces first headache, drowsiness, stupefaction ; if inhaled for a long time, death.

CHAPTER XV.

CARBON COMPOUNDS; ORGANIC BODIES.

WE discovered in the lime gas the oxyd of a peculiar element which we named carbon from its resemblance and action to charcoal. As element we find carbon among minerals in two forms: as diamond and as graphite. Diamond is the hardest, graphite the softest of all minerals. Both resist all agents with energy. A yellow heat is required to enable oxygen to combine with adamantine carbon as well as with graphite carbon. It was a great feat to even suspect that diamond was merely crystallized carbon. Isaac Newton concluded that diamond must be a combustible substance, on account of its high index of refraction. The Academy of Florence in 1694 showed by experiment that diamond disappears in the focus of a large lens. Lavoisier showed, in 1786, that lime gas results from the burning of diamond, and Humphrey Davy, in 1807, proved it to be pure carbon. No attempt at making diamond artificially has been a success, up to this time, and it is not known by what way Nature arrives at the product. That diamond has been found in meteoric iron together with amorphous carbon (Koenig, 1889) indicates a high temperature as one of the conditions. On the other

hand the perfect crystals found in flexible sandstone in Brazil indicate a low temperature as one of the conditions.

Graphite is of very common occurrence in the archean rocks either in mica schist or in white crystalline limestone. Sometimes large bunches together, but mostly in isolated scales. Graphite forms in pig-iron, also in gas retorts at high heat. It burns more readily than diamond, especially in oxygen gas. Long boiling with fuming HNO^3 converts it into a yellow substance which has been named graphitic acid.

The *mineral coal* cannot correctly be named carbon, not even the finest anthracite of Pennsylvania; it contains however up to 95 per cent. of carbon. The great storage of carbon in the earth must be looked for in the limestones; and in the air, though the percentage of carbon dioxyd in the atmosphere be but 0.02 per cent. Yet all this immense quantity of carbon is of very little value to mankind. As CO^2 it is equivalent to *spent energy*, to an uncoiled spring. At this point intervenes *organic life* contained in the animated *cell* filled with that most mysterious substance, the *protoplasm*. Under its influence carbon dioxyd is split up into carbon and oxygen, a part of the oxygen returns to the air, the remainder together with carbon and hydrogen serving in building up the body of the plants.

THE COMBINATIONS OF CARBON AND OXYGEN.

We saw that the limestone gas is an oxyd of carbon, and furthermore that this oxyd changes into a combustible oxyd by the action of zinc and heat. There are then two oxyds of very differing properties. Being now in possession of the required knowledge we will proceed to the properties and composition of these oxyds.

Carbon dioxyd, CO^2, often erroneously named *carbonic acid.* This is our limestone gas as well as the gas evolved from all carbonates by the addition of HCl or any other so-called acid. This is a substance of fundamental importance, and its properties should be memorized by any engineer, because what is called perfect or complete combustion means nothing but the conversion by burning of carbon into CO^2, and because by this combustion the highest heat-value is obtained from coal or any other fuel.

Physical properties. Carbon dioxyd is a colorless gas without odor; but it gives to water a pleasant, prickling taste. Its specific gravity is 1.524, hence the gas is found near the floor when it issues into the workings of a tunnel, shaft, or other mine-working, or in caves such as the *dog-cave*, where a dog dies rapidly, while a standing man, alongside, breathes freely. It spec. heat is 0.22 (water $= 1$), 1 liter at 0° C. weighs 1.97 grams. The gas can be liquefied at the freezing-point of water under a pressure of 38.5 atmospheres; at 31° C. a pressure of 74 atmospheres is required. If two strong metallic

vessels (cylinders) be connected by a flexible metallic tube, and if one vessel has been previously charged with sodium-hydrogen carbonate and sulfuric acid in such a way that the agents only come together when the cylinder is tilted, then pure CO_2 will be generated, and not being able to escape, it will liquefy in the second cylinder under its own pressure. The temperature rises to 40° C., so that upon screwing a metallic receiver upon the second vessel, the liquid CO_2 will distill into the receiver and the temperature will drop quickly to about −80° C. and solidify into white crystal-flakes like snow. (Application as a very intense freezing mixture.) Liquid CO_2 is colorless and mobile, its specific gravity at ordinary temperature being nearly that of water. CO_2 is quite soluble in water at ordinary temperature, and much more so under pressure. The sparkling or boiling cold-springs, as well as the artificial soda-water are charged with the gas under pressure and release it when the pressure is taken off. If air be mixed with 4 vol. per cent. of CO_2 it becomes unfit for the proper oxygenation of the blood in the lungs. In larger proportion it *suffocates* at once. Note ventilation of rooms and mines on this account. The poisonous action is negative.

Chemical properties. Moist litmus paper will turn to a reddish-purple in a test-tube which has been filled with the gas. We assume (without proof) that the water-solution contains a weak acid $H_2O.CO_2 = H_2(CO_3)$. The gas is eagerly absorbed

by $NaHO$, KHO, $Ca(HO)_2$, $NH_4(HO)$ and even by Na_2CO_3 which changes into $2NaH(CO_3)$. These latter actions we utilize for the identification of the gas, for its abstraction from a mixture of gases in gas analysis. Because if the white precipitate of $Ca(CO_3)$ be filtered off and then be acted upon by dilute HCl solution, a colorless and odorless gas will be evolved which can only be CO_2, for SO_2 and N_2O_3 are each pungently odoriferous.

Composition of CO_2. If a piece of purest charcoal be placed in a knee-tube over mercury (see proof of SO_2), the tube be partly filled with pure oxygen, and the coal heated to redness it will burn with a bright light. When the temperature has returned to normal the volume of gas is unchanged. Hence 1 volume CO_2 contains 1 volume O.

But 1 volume CO_2 weighs 1.965 grams.
1 volume O weighs 1.429 grams.
—————
0.536 grams.

hence 0.536 is the weight of carbon which has entered into combination. We know that the gas is CO_2 for it is completely absorbed by introducing a drop of $NaHO$ solution. Unfortunately carbon is practically non-volatile at feasible temperatures, hence we are ignorant of the weight of one volume of this element. But since CO_2 and SO_2 are in many ways similar and because we did prove in the case of SO_2 that the difference between the weights of equal volumes of SO_2 and oxygen is equal to $\frac{1}{2}$ volume of sulfur, therefore we can assume that 0.536

equals the weight of $\frac{1}{2}$ volume of carbon, and hence our gas contains in one volume

$$1 \text{ vol. } O + \frac{1}{2} \text{ vol. } C, \text{ and}$$
$$2 \text{ vols. } CO_2 = 2 \text{ vols. } O + 1 \text{ vol. } C$$
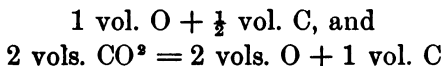
a contraction of 3 to 2.

On the other hand it has been found by burning a known weight of diamond, that 1 gram of the latter (pure carbon) yields 3.666 grams of CO_2, therefore in it are combined C 1.00 with O = 2,660. Having previously found that the volume ratio is CO_2 we arrive now at the atomic weight of carbon, C by the proportion $\dfrac{2,666}{2 \times 16} = \dfrac{1}{C}$ or $C = \dfrac{1}{0.8331} =$ 12.003. *The atomic weight of carbon is 12.* The weight of 1 volume carbon vapor is 1,072. The molecular weight of $CO_2 = 44$.

Carbon monoxyd, CO, sometimes called *carbonous oxyd.* This gas may be generated in numerous ways of which the most ordinary is the passing of dry CO_2 over well ignited charcoal at a red heat. Use the apparatus given under lime gas, substituting the charcoal for the zinc. Let the resulting gas pass through solution of NaHO which will absorb any CO_2 that may have escaped decomposition. It will be seen that for every bubble of CO_2 passing into the charcoal, there will be two bubbles of carbon monoxyd coming out.

$$1 \text{ vol. } CO_2 + C = 2 \text{ vols. } CO.$$
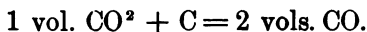
This gas always generates when any fuel burns imperfectly, that is when there is a lack of oxygen.

If you observe an anthracite stove fire sometime after fresh coal has been added (opening the charging door) you will see *blue* flames bursting out all over the coal. This is very characteristic of CO— that is $CO + O + heat = CO_2$ with blue flame. Carbon monoxyd explodes with $\frac{1}{2}$ volume of oxygen or $2\frac{1}{2}$ volumes of air. It can therefore be used in gas engines.

The gas is neutral, has a gravity of 0.967, is only liquefiable at —139° C. and a pressure of 35.5 atmospheres. It freezes at —207° C. It is little soluble in water. It is very poisonous in a positive way inasmuch as it combines with the red corpuscles of the blood, changing the color to purplish. As such it is the worst enemy to the rescuing parties who enter a coal mine after an explosion, since the combustion is usually imperfect and the gas has nearly the same gravity as air. The charcoal poisoning is due to this gas; or, any boiler-room may become deadly from it if the draft should stop on reverse ; its presence cannot be told by the odor. CO is quite eagerly absorbed by solutions of *cuprous chlorid* Cu_2Cl_2 either in HCl or in $NH_4.HO$. (Use in gas-analysis.)

Proof that composition is CO. Bring into a eudiometer over mercury 1 volume of the gas $+ \frac{1}{2}$ volume of O and explode. There will be left 1 volume of CO_2, it follows that 1 volume of CO contains the same volume of carbon as 1 volume of CO_2. But we saw above that 1 volume of CO_2 contains 1 volume of O, hence 1 volume CO contains $\frac{1}{2}$ volume of C $+ \frac{1}{2}$ volume of O.

STRUCTURE OF PLANTS.

The structural unit of the plant is the *cell*. The natural shape of a plant or animal cell is the sphere, *A* (Fig. 74). When cells crowd each other in an aggregate, their shape becomes polyhedral, *C* (Fig. 74). When crowded only in one direction the cell is apt to become an elongated bag—cotton or linen fiber, *B* (Fig. 74). Each live cell has three

Fig. 74.
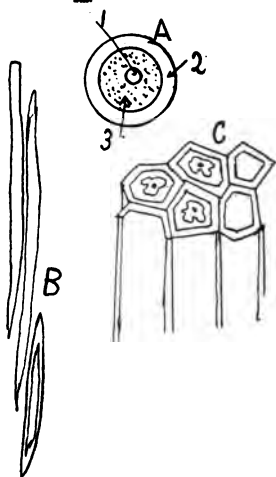
essential parts : The cell wall, *A2*, the nucleus, *A1*, the sap or protoplasm, *A3*, filling the cell space. From 80 to 90 per cent. of the sap is merely water. The substance of the cell wall is named *cellulose*. Since the body of the plant is made up of root, stem, branches, leaves, the flowers being merely modified leaves, and since all these are made up either

of live or dead cells, it follows that a plant, after
the sap is dried out, is practically nothing but cel-
lulose, with more or less secondary substances, such
as starch, coloring matter, resin, which had been
dissolved in the sap or had exuded from the cells
into the intercellular space. Wood is impure
cellulose. The purest form of cellulose is cotton,
pith, paper pulp. Cellulose enters into so many
applications, and forms as wood one of the engi-
neer's sources of fuel, that we must devote some
time and exertion to its study.

Let some cotton, or filter paper, be dried at 105°
C. in an air-bath until its weight shall have become
constant. We need not try whether it will burn;
we know it will. But let us contrive to burn it
completely in such a way that the products of the
combustion can be collected and weighed. The pro-
ducts of the burning are flame and ashes. Flame is
a mixture of gases. These gases we must collect.
We do this first so that we may study the kinds
(qualitative) of elements in the gases, and then,
in a more guarded experiment, the quantities.

(1). We burn 1 gram in a crucible. A very small
quantity of ashes remains. The ashes partly soluble
in a little water, show alkaline reaction, and effer-
vesce with HCl—(K^2CO^3). This potassium carbon-
ate was not originally in the sap; the potassium
was combined with the carbon acids, which we will
consider hereafter. Combustion converts these salts
into the carbonate.

(2). We burn 1 gram in an open tube and draw

(by means of an aspirator) the gases through water. The latter does not acquire acid reaction, hence sulfur and chlorine are not contained in the cellulose. While the substance burns we note the deposit of water in the cool end of the tube, therefore the cellulose contains *hydrogen*. We draw a part of the burning gases through a tube filled with lime water and note a strong white turbidity appearing showing the presence of *carbon* in the cellulose.

(3). We mix a gram of the substance with soda-lime ($CaCO^3 + 2Na(HO)$) and heat in a tube closed at one end—no smell of *ammonia* is noticed. Moist, red litmus held into the open end does not turn blue, hence *nitrogen* is absent, and thus we have proved that cellulose consists merely of C^m, H^n, O^p.

And now we proceed to find the numerical values of m, n and p. By experiment we know that when hydrogen passes over CuO at red heat H^2O will be formed and metallic copper. Similarly CuO heated with charcoal will give metallic copper + CO. And if CO be passed at red heat over CuO it will give Cu + CO^2. Upon these facts we can now contrive a process and suitable apparatus for the purpose in hand.

In Fig. 75 the hard, infusible glass tube *T*, 20 inches long, ⅝ inch wide, is furnished with perforated stoppers, and is placed into the sheet-iron charcoal furnace *F*, being supported the entire length by a half cylinder of iron, thus preventing sagging and deformation. The tube is charged at *1* with 3 inches of coarse copper oxyd, then comes 10 inches

of copper oxyd with which has been intimately
mixed the cellulose (0.5 gram cut up with scis-
sors). Then comes at *3*, 5 to 6 inches of coiled
copper gauze, which has been partly converted
into CuO by heat and oxygen. Everything must

FIG. 75.
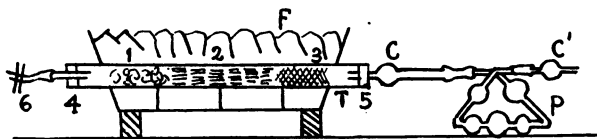
be thoroughly dried before charging, as we de-
sire to catch and weigh the water formed by the
combustion. Into the stopper *5* fits the bulb-tube
C, filled with pieces of $CaCl^2$. To this tube is
joined by a short rubber connection the bulb-tube
P, known as a Liebig *potash bulb*, and to this is
joined a second smaller bulb-tube *C'* filled with
$CaCl^2$. Through stopper *4* passes the inlet tube
with rubber tube and spring clamp *6*. The rubber
tube leads to a holder for air with tubes for drying
and purifying the air. The tubes are filled with
Na(HO) in pieces to retain CO^2, which is always
in the air, and $CaCl^2$ to take up the moisture.
The bulb *P* is partly filled with a 1:3 solution of
NaHO in water. First we weigh the tube *C* by
itself, and $P + C'$ together. During the process of
weighing, the tubes *C, P, C'* are air-tightly closed
by means of pieces of rubber and glass rod. Let
the weight of $C =$ a grams, the weight of $P + C' =$

b grams.　After all is again joined, open the clamp *6*, so that bubbles will be seen to rise in the liquid of *P;* the level in the farther bulb will rise until the bubbles can pass from the middle bulb through the joining neck.　The bubbles should pass at the rate of one per second.　Now we place a sheet-iron diaphragm in the furnace, astride the tube *T*, just where the copper gauze begins, heap in first some ignited pieces of charcoal, then black pieces, and help the fire by gentle fanning.　When the tube and gauze are red hot remove the shield or diaphragm 2 inches to the left, and even up the coal. Every 10 minutes move the shield 2 inches further to the left, until we have reached the left end of the furnace, and then keep up a uniform red heat for 10 minutes more.　The cellulose is burnt up by this time, and the products of the combustion have been carried forward into the absorption tubes by the slow current of air.　It may be that a small quantity of water still lingers this side of *C*.　We draw *T* to the right to heat the end of it and cause the water to evaporate and to get into *C*.　Now we detach first *P* from *C*, put on the glass plugs, then draw out *C* and put on the plug.　Then we weigh. The weight of *C* will now be a' grams, that of $P + C'$ $= b'$ grams; the increase in *C* being due to water, the increase in $P + C'$ being due to carbon dioxyd. Having started with 0.5 gram of cellulose

$$a' — a \text{ will be } 0.2772 \ H_2O$$
$$b' — b \text{ will be } 0.8147 \ CO_2$$

$$\frac{H^2}{H^2O} = \frac{1}{9}; \quad H^2 = \frac{H^2O}{9}; \text{ hence } 0.2772 \ H^2O =$$
$$0.0308 \ H$$

$$\frac{C}{CO^2} = \frac{3}{11}; \quad C = \frac{3}{11} CO^2; \text{ hence } 0.8147 \ CO^2 =$$
$$0.2222 \ C$$

0.5 gr. cellulose contains 0.2222 C; 0.0308 H; 0.2470 O.

For the difference $0.5 - 0.2222 - 0.0308 = 0.2470$ must be oxygen, we have proved by the experiments above, that cellulose can contain only C, H, O. Expressed in percentage we get

$$C = 44.44$$
$$H = 6.16$$
$$O = 49.45$$

Dividing these percentages by the atomic weights we obtain the atomic quotients thus,

$$\frac{44.44}{12} = 3.7033$$

$$\frac{6.16}{1} = 6.1600$$

$$\frac{49.45}{16} = 3.0906$$

We reduce these to units of oxygen, because oxygen has the smallest quotient,

$$\frac{3.7033}{3.0906} = 1.198 \text{ or } 1.20$$

$$\frac{6.1600}{3.0906} = 1.993 \text{ or } 2.00$$

$$\frac{3.0906}{3.0906} = 1.000 \text{ or } 1.00$$

and obtain the nearest whole numbers which are 12 — 20 — 10. But these numbers are divisible by 2, therefore in the molecule of cellulose the three elements are contained in the ratio

$$C^6H^{10}O^5 = \text{cellulose}$$
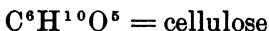
The weight of the molecule is $6 \times 12 + 10 \times 1 + 5 \times 16 = 162$

The first point striking our attention is that hydrogen and oxygen are in this molecule exactly in the same ratio as that of water, so that we might write the formula $C^6(H^2O)^5$, a *hydrate of carbon.* As there are a number of other bodies of this type it is well to distinguish them as a group by the name *carbon hydrates*, although we know well that $H + O$ are not grouped in the molecule as H^2O. For if they were, the cellulose would have to part, on heating, into $C + H^2O$, but it does so only in part as we shall see presently in the destructive distillation of wood.

Some of the Properties of Cellulose or Wood Fiber.

It is colorless or white. It is insoluble in water, in alcohol, in ether, whether cold or boiling. It is not affected by dilute solutions of the alkalies and acids at ordinary temperatures. Persistent boiling with these dilute agents slowly dissolves it.

Vegetable parchment = papyrine, results when good filter paper is immersed for a few seconds into a mixture of 1 vol. conc. $H^2SO^4 + \frac{1}{2}$ vol. water. After withdrawing the paper from the acid it must

be washed out with much water and finally with a 2 per cent. solution of ammonium hydrate, to remove every trace of adhering acid. It is then dried. After drying, water has little effect upon it; it does not blot, and resembles dried skin.

Nitro-cellulose, gun-cotton, $C^6H^7(NO^2)^3O^5$, *tri-nitro-cellulose.* Let cleansed, dry cotton be immersed for 5 minutes in a liquid consisting of 1 vol. fuming $HNO^3 + 3$ vols. conc. H^2SO^4. Let it then be squeezed out and thrown into much cold water and washed until all acid reaction has disappeared. On drying we find that externally the cotton has retained shape, color and cell structure; its weight has increased 50 per cent., its tensile strength has considerably decreased. But it has acquired the faculty to explode with great force, when struck a sharp blow with a hammer upon an anvil. Ignited by a match it burns instantly with a flash but without detonation. If the material be put into a closed space, such as a drill hole, and then ignited it will rend the enclosing material·same as gunpowder.

Explanation. Analysis shows that the composition of the altered cotton leads to the formula $C^6H^7N^3O^{11}$, the substance having become a *nitro body*. Three atoms of hydrogen have been removed from the cellulose and in their places have been substituted $3N + 6O = 3NO^2$. We can represent this graphically thus:

$$C^6H^7 \underset{\diagdown}{\overset{\diagup}{\underset{\text{H}}{\overline{\text{H}}}}} O^5, \text{ Cotton or cellulose;}$$

$$C^6H^7 \begin{matrix} \diagup NO^2 \diagdown \\ =NO^2= \\ \diagdown NO^2 \diagup \end{matrix} O^5, \text{ Trinitrocellulose.}$$
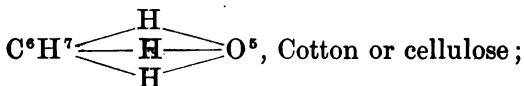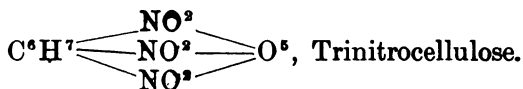
The change can be represented by the equation:

$$C^6H^{10}O^5 + 3HNO^3 = C^6H^7(NO^2)^3O^5 + 3H^2O$$
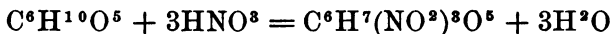
There is no evolution of gas. The water is taken up by the concentrated H^2SO^4 and the HNO^3 suffers no loss of energy through dilution. If ordinary conc. HNO^3 be taken, a different product results. It appears the same to the eye, but dissolves in a mixture of alcohol and ether. The product is essentially $C^6H^8(NO^2)^2O^5 = $ dinitrocellulose. It bears the name *pyroxyline* and its ether-alcohol solution is called *collodion*. Collodion produces a transparent film when allowed to run over a clean glass plate. This is the film used in the *wet plate* process of photography. It is also used in surgery to keep a fresh wound from contamination with the poison microbes of the air.

Gun-cotton (trinitrocellulose) as an explosive. The products of the detonation of gun-cotton are $CO + N + CO^2 + H^2O$. Two molecules will give $9CO + 3CO^3 + 6N + 7H^2O$.

1 molecule $C^6H^7(NO^2)^3O^5$ weighs $72 + 7 + 138 + 80 = 297$.

$2 \times 297 = 594$ grams of $C^6H^7(NO^2)^3O^5$ give $250CO + 132CO^2 + 84N + 126H^2O$. 1 gram of $C^6H^7(NO^2)^3O^5$ gives $0.4242CO + 0.2222CO^2 + 0.1414N + 0.2121H^2O = 0.9999$ substance.

Since 1 c.c. CO weighs at 0° C. (760 mm)
$$= 0.00125 \text{ gr.}$$

    1 c.c. CO_2 $= 0.001977 \text{ gr.}$

    1 c.c. N $= 0.001256 \text{ gr.}$

    1 c.c. H_2O (steam) at 100° C. $= 0.000589 \text{ gr.}$

Therefore 0.4242 gram CO occupy the space of
$$\frac{0.4242}{0.00125} = 339 \text{ c.c.}$$

0.2222 gram CO_2 occupy the space of
$$\frac{0.2222}{0.00199} = 112 \text{ c.c.}$$

0.1414 gram N occupy the space of
$$\frac{0.1414}{0.001257} = 113 \text{ c.c.}$$

0.2120 gram H_2O occupy the space of
$$\frac{0.2120}{0.0005896} = 360 \text{ c.c.}$$

But the volume V, equal to $(339 + 112 + 113) =$ 564 c.c. of $CO + CO_2 + N$ at 0° C., will be at 100° C. equal to $564 + (564 \times 0.37) = 772$ c.c., and the total gas at 100° C. $= 772 + 360 = 1132$, or over three times the volume of the gases which are evolved from 1 gram of black powder. Assuming that 1 gram of gun-cotton fills the space of 1 c.c., and that the sensible temperature of the gases after explosion be 1000° C., after proper deductions for loss, the pressure exerted by the gases will then be (for the permanent gases alone) $772 + 285 = 1057$ atmospheres per 6 sq. centimeters. For the aqueous vapor we get, at the least, a pressure of 360 atmos-

18

pheres per 6 square centimeters, a total of 1417 atmospheres pressing upon 6 square centimeters.   1 square inch $= 6.452$ square centimeters.   Hence we get $1417 \times 15 = 21255$ lbs. pressure on one square inch nearly.   When used in underground workings the air becomes poisoned, partly by the carbon monoxyd, but chiefly from the brown niter gases, NO^2.   This shows that the explosion does not break up the gun-cotton always alike.   NO forms instead of CO^2, and then after explosion, when the gases mix with the air, NO becomes NO^2.

THE ACTION OF HEAT UPON CELLULOSE.   DESTRUCTIVE DISTILLATION OF WOOD.   CHARCOAL MAKING.

Let a splinter of dry wood be heated over an open flame, in a narrow glass tube which has been closed at one end.   We notice the wood burning first yellow, then brown, then black, while a dense yellow vapor is evolved.   The vapor condenses partly into a brown-red liquid.   The vapor escaping from the tube burns, is inflammable.   In order to study each of these three main products, one must repeat the experiment on a larger scale, and so that the products may be completely collected, especially the gas.   The following arrangement of apparatus Fig. 76 will answer and yet be simple.

A strong glass tube T closed at one end lies in a furnace F as in the previous experiment.   The tube holds a stick of dry wood 20 grs. in weight.   The tube T reaches into a glass receiver R, home-made from a large test-tube.   A rubber band 2 makes this

connection tight. B is an open bell jar with stop-
cock 6 connected by angle tube 5 and rubber tube 4
with the receiver.   The bell stands in a large beaker
glass H, two-thirds full of water.   With open stop-
cock 6 and sucking at the rubber tube 4 the bell is
filled with water; the stop-cock 6 is then closed.
Live charcoal is piled into the furnace to the left of
the shield S.   The distillation begins; the gases
drive the air out of 7 and R.   As soon as the yel-
low cloud fills R, we connect the rubber tube 4 with
R, and by so doing will have fair assurance that

Fig. 76.
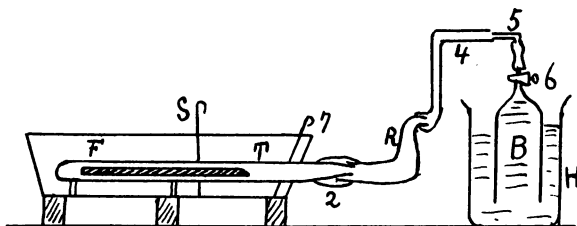
whatever gases are now collecting in B will have
been produced from the breaking up of the cellulose
molecule.   Care is taken to give T a slight inclina-
tion forward, to wit, by raising the closed end.   The
condensed liquid will then run into R, and not back-
ward, where it might cause a breaking of red-hot
glass.   When the flow of gas becomes slower we
move S into the position 7, and fill in fresh live coal.
Be watchful of the glass tube T.   If its temperature
rises above cherry redness it is apt to bulge out, be-
come weak and perforated, an event which prema-

turely ends the experiment. We maintain the heat until the volume of gas in B becomes stationary. All this time we have been lifting the bell B so that the liquid *inside* remained higher than the outside level, which means a steady suction or partial vacuum. The latter is an additional precaution against the distention or bulging of the softened, red-hot glass tube. If now a mark is made upon the bell to indicate the height of the level when water stands evenly inside and outside, (the coal being removed and the tube having acquired ordinary temperature) we will have the volume of gas V which can be obtained from the distillation of 20 grams of dry wood. We then close the stopcock $6'$, and set aside the bell and holder. We detach the receiver and weigh it with contents, then without contents, and thus find the weight of the latter. Lastly we take out the charcoal from the tube and find its weight.

(1) *The charcoal.* Varies in color from red-brown to deep black, according to the temperature. The higher the heat, the deeper the black. The brown charcoal is imperfectly done, as shown by the following analysis: C, 70.4 ; H, 4.6 ; O, 24.2 ; ashes, 0.85.

But even the hardest and blackest charcoal is not all carbon ; temp. 1300° C.: C, 90.8 ; H, 1.6 ; O, 6.5 ; ashes, 1.15.

(2) *The brown liquid.* Even in the receiver, R, one notices that the liquid consists of two parts ; one watery, *mobile*, brown liquid, we designate *pyro-*

ligneous acid; the other portion, dark black-brown, viscous, not very liquid, shall be named *wood-tar.* Both portions possess a penetrating, peculiar, not unpleasant odor—the odor of smouldering wood, *empyreumatic odor* from Greek, fire odor. The taste of both portions is bitter, unpleasant. Some of the tar collects over the pyroligneous acid, some at the bottom, and some remains suspended. This proves tar to be a mixture of several bodies. The pyroligneous acid is so named because of its acid reaction on litmus, and from *pyro,* fire; *lignum,* wood, *firewood acid.* Let the two portions be separated by filtering through charcoal powder which lies in a cotton-plugged funnel. The tar particles adhere to the charcoal, pyroligneous acid passing through. We add solution of NaOH until the acid reaction on litmus ceases. We bring the liquid into a flask with perforated stopper, a glass tube, bent over so as to connect with a cooling tube, passing through the hole. On boiling, a colorless liquid passes over which shows the strong odor still very markedly. But the liquid is inflammable; its specific gravity is less than water. This substance is known as *wood spirits.* A closer study reveals that this liquid may be separated by fractionating into water plus concentrated spirits, and the latter again fractionated gives the pure wood spirits, also known as *wood alcohol; methyl alcohol.* It is a very mobile liquid, which boils at 60.5° C. Its specific gravity at 4° C. = 0.81 (water = 1). Mixes with water in all proportions. Burns with bright bluish hot

flame. It is very useful in the chemistry of dye-stuffs as a solvent and modifying agent.

The analysis gives for it the symbol CH^4O. We evaporate the remaining liquid in a boiling flask to dryness. A black mass results which we calcine in a porcelain dish, that is heated over the open flame until the black color has become grey-oily; gases and vapors pass off. We return it then to the distilling flask with H^2SO^4 and water. A colorless liquid condenses, very mobile, very sour. Because, we reason, if the original acid in the pyroligneous liquid be HA then by adding NaHO we get $NaA + H^2O$. Then acting with H^2SO^4 must give us

$$2NaA + H^2SO^4 = Na^2SO^4 + 2HA \text{ (the new acid)}.$$

The analysis gives for HA the formula $H.C^2H^3O^2$. We name it *acetic acid* from *acetum* = Latin for vinegar, for the acid resulting from the fermentation of fruit juices has the same composition and properties as this wood acid. Acetic acid $H.C^2O^3O^2$—short symbol, $H\bar{A}$—is a liquid, colorless mobile; with very sharp odor. At 0° C. this liquid acid becomes solid, crystallizes ; and strangely these crystals only melt at 16° C., having sp. gr. 1.0553. This most concentrated acid is known as *glacial* acetic acid. When water is mixed with this glacial acid, the specific gravity *increases* although the water is less heavy. This can only be explained by assuming that the molecules of the strong acid are in their free state farther apart than in the water-mixed state, that the addition of water causes the drawing together of these molecules. The spe-

cific gravity increases until 22 parts of water have been added to 78 pts. of acid, when the specific gravity = 1.0748. Beyond, with more water the specific gravity decreases. A mixture of acid 43, water 57 has again the same specific gravity as the pure acid. H$\bar{A}$ forms salts with all metals except gold; and the normal salts are all *easily soluble in water*. The *acetates* are much used in dyeing, especially Pb($\bar{A}$)^2 and Al($\bar{A}$)^3. In the manufacture of charcoal, the pyroligneous acid is neutralized with Ca(HO)^2 slaked lime, in place of Na(HO) because cheaper. Hence the crude Ca($\bar{A}$)^2 is the product of commerce, shipped from the woods to the large cities, where the acid itself is then distilled.

(*3*) *The tar or wood tar.* It has been stated above that by this name is meant the oily dark-colored material which either rises as a scum to the top of the wood acid, or sinks to the bottom of the latter. We separate it from the watery liquid and proceed to its examination. The expression Tar-jacket for a sailor came in use through someone's observing that the steeping of wood or linen in tar, made those substances impervious to water, and prevented both dry-rot and wet-rot (the decaying of wood). Hence the practice rose to soak the wooden planks of boats and ships with the tar, also the entire rigging, especially halyards and shrouds and cables, also the overalls of the sailors, with this strong-smelling material. Later on fence posts, telegraph poles, etc., were steeped, and lastly, railroad ties.

Evidently mine timber would be benefited by
means of repeated coats of tar, wherever mines are
half wet, and the timbers succumb rapidly to the
rot, *i. e.*, fungus and microbes.   The curing of hams,
bacon, fish, by first salting and then drying them
out over a smoking, smouldering wood fire, is a very
ancient practice.   The tar oils condense on the sur-
face of the meat and keep off the microbes of putre-
faction until the meat is dried out and no longer

FIG. 77.
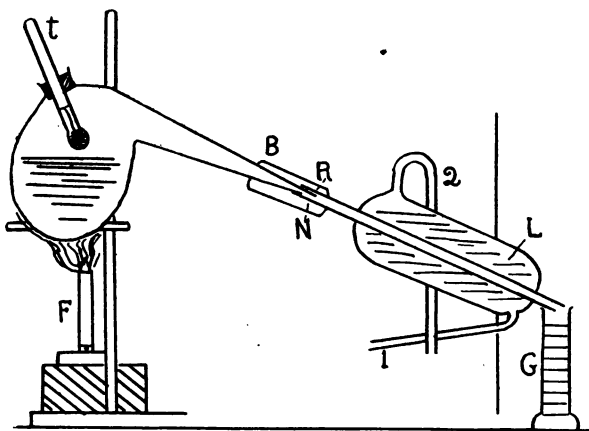
subject to the action of these organisms.   Tar burns
freely and is used as a so-called liquid fuel.   Let
the tar be heated in a retort, which is furnished
with a thermometer, Fig. 77, *t;* the neck of the re-
tort reaching by a reducer *B*, the tube of a Liebig
cooler *L*, the joint *R-N* made tight by a rubber
band.   Cold water enters from a hydrant through

connecting rubber *1* into the cooler, the warm water
leaving through rubber tube *2*. The flame from
burner *F* is so regulated that the liquid keeps gently
boiling. We notice that the mercury in thermometer
will be steadily rising, while a clear liquid collects
in the graduate *G*. The rising thermometer can
mean two things: (a) The tar is a mixture of
liquids having their boiling points at different tem-
peratures. (b) The tar is a uniform chemical sub-
stance, which, however, breaks up by the heat into
bodies of different boiling points. Evidently it
makes no difference for practical purposes whether
the truth lies in condition (a) or whether it lies in
condition (b). If the graduate *G* be emptied when
10 c.c. have been condensed, and so every other 10
c.c. be collected separately (distillation by fractions),
it will be found that the specific gravity of each
fraction is higher than that of the preceding fraction,
varying from 0.82 to 0.87. Before the Pennsylvania
coal oil had come into general use, these tar oils
took the place as illuminating agents, the lighter
part going by the name of *photogen*, while the heavier
part was known as *solar oil*. To the latter clung the
strong penetrating odor. If this portion be shaken
with NaOH or KOH in water-solution for some
time, and the two liquids be allowed to stand
quietly, they will separate, the oil above, the KOH
water-solution below. In a separatory funnel the
aqueous liquid can be drawn off clean. We make
acid with dilute H_2SO_4, and find again an oil
separating at the top. This oil possesses a penetrat-

ing odor, and a bitter astringent taste.   It used to be called *creosote,* is now called *carbolic acid* or *phenyl hydroxyd.*   The combustion analysis (refer to cellulose) gives the ratio of the elements as C^5H^6O, but because this body as we have seen combines with KOH, and because it also dissolves in strong H^2SO^4, we write its formula, $C^6H^5(HO)$. C^6H^5 as radical we call *phenol* or *phenyl.*   Towards strong bases it acts as an acid, towards strong acids as a base. Thus :

$$KOH + C^6H^5(HO) = H^2O + (KO)C^6H^5, \text{ potassium carbolate.}$$

$$2C^6H^5(HO) + H^2SO^4 = C^6H^5.H(SO^4) + H^2O = \text{ phenyl sulfate + water.}$$
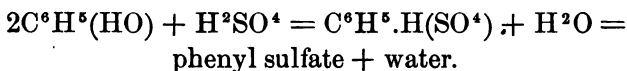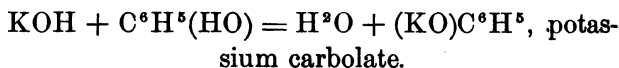
Carbolic acid or *creosote* is at ordinary temperature a crystallized solid without color, but possessing a strong smell.   It melts quickly into a thick oil. One part dissolves in 10 parts of water.   It is very poisonous to animal life.   It is used as a germ-destroyer, but its chief use is to act as base for the manufacture of *picric acid.*   Coal-tar contains more carbolic acid than wood-tar.

Trinitrophenol, $C^6H^2(NO^2)^3OH$, *picric acid.*   Take about 1 c.c. of liquid carbolic acid.   Pour this into 10 c.c. of fuming HNO^3.   The action is apt to be violent, copious brown fumes being formed.   Boil until brown fumes stop.   Then pour liquid into much cold water.   The water takes a deep yellow color and a yellow sediment falls out.   The yellow substance is picric acid.   Pour off the yellow

liquid and add to the residue again about 50 c.c. of
water, and boil. The picric acid being more soluble
in boiling water, a brown resin-like substance re-
mains. As the boiling yellow liquid cools down it
throws out yellow, scaly crystals, the picric acid;
picros = bitter, on account of the strong bitter taste.
Solution reddens litmus; can be neutralized with
KOH or NH⁴HO when yellow needles fall from the
solution, representing the potassium, or ammonium
picrate. Both these salts are very explosive, more
so than the acid itself. The ammonium picrate is
used in the smokeless powders.

$$C^6H^2(NO^2)^3HO + NH^4HO = (NH^4)O.C^6H^2\text{-}$$
$$(NO^2)^3 + H^2O.$$
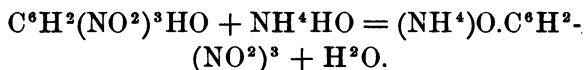
The solution of picric acid is used in dyeing silk and
wool a beautiful golden-yellow color.

Paraffin, $C^{17}H^{36}$ to $C^{24}H^{50}$. On continuing
the distillation of the tar, after the solar oil sp. gr.
0.86, we find that the vapors condense in the tube to
a semi-liquid, buttery product, and finally they con-
dense to a rigid solid. By pressing the semi-liquid
between paper, we find scaly crystals in the paper
and a liquid pressed through the latter. The liquid
is known as *paraffin oil* for lubrication, and the crys-
tals go under the name of *paraffin.* So also does the
material which solidifies at once into a rigid solid.
After refining, the paraffin is used for *imitation wax*
candles. As given above, the solid is not a homo-
geneous body, but a succession of hydrocarbons of
the general formula C^nH^{2n+2}. The melting-point is

the arithmetical mean of those of the different members.

Paraffin is useful in the laboratory to soak corks in, to paint over labels with, and in fact to cover all metallic apparatus which is not subjected to heat, for it is a body very indifferent to chemical action.

Only hot concentrated HNO^3 or hot H^2SO^4 will decompose it.

Examination of the wood gases. In this examination we make use of the solubilities of the gases in

FIG. 78.
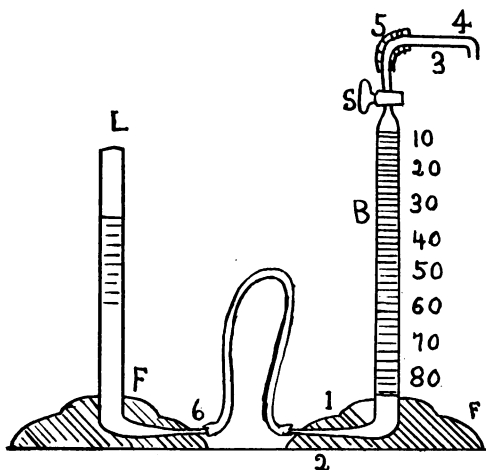
liquids or their absorption by solids. The sum of the processes we designate as *gas analysis.* The most convenient apparatus for the purpose has been designed by Professors Winkler and Hempel; though a number of others of no less ingenuity have con-

tributed their share.   In Fig. 78 *B* represents the *burette* or measuring vessel, a cylindrical glass tube graduated into 100 c.c. and $\frac{1}{5}$ c.c.   The tube stands in the cast-iron foot *F* so that it will not be upset easily.   *F* is bored out at *1* to admit a small tubulature to which a strong rubber tube is wired.   The stop-cock *S* has a capillary perforation which leads to the capillary tube *3*.   With the latter is united by the wired rubber *5* the *capillary* transfer tube *4* in form of a double L.   The hollow volumes or canals of both tubes do not exceed 0.01 c.c.   *L*, Fig. 78, is the *level tube* in foot *F* to which the rubber tube from foot of *B* is joined and wired at *6*.   The rubber tube should be as long as the cylinder is high, so that the foot of one cylinder may be raised to the top of the other cylinder.   This arrangement permits the reading of the gas volume under constant pressure, *i. e.*, the pressure of the atmosphere, and in so much as the temperature of the room does not materially change during one set of absorptions, we may set down the temperature as constant and thus avoid the reductions of volumes to 0° C. and 760 mm.

Fig. 79 shows the pipette or absorption vessel for absorbing CO_2.   The glass bulb, *C*, is seen filled with small coils of iron wire gauze, which are introduced by means of the wide mouth and stopper at *S*.   This bulb communicates through tube, *1*, with the reservoir-bulb, *D*, which is open at the top.   A capillary glass tube leads in single loop to the rubber tube, *3*, the latter being closed by the pinchcock, *4*.   The whole combination is fastened to the

iron frame, *F*, which has taken the place of the former wooden frame, the spilling of the strong agents over the wood making it soon unsightly and insecure to stand up. The absorbing liquid is a solution of 15 grams of KOH or NaOH in 50 c.c. of water. This solution is poured into *D* (pinch-cock being open); the air is forced into *D*, the pressure driving the liquid gradually through the capillary

FIG. 79.
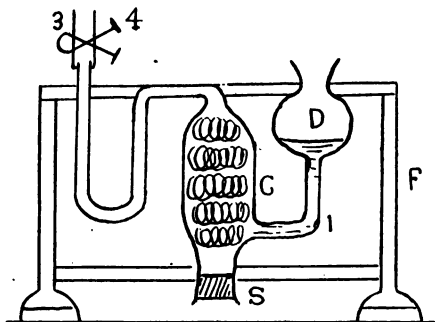
tube leading to *3*, until the liquid appears at the top of *3*. The coils of iron wire gauze being moistened with the alkali, expose a very large surface to the gas and cause an almost instantaneous absorption of the CO_2.

Fig. 80 represents a *double pipette*, to be used for liquids which are easily deteriorated by the oxygen of the air, like potassium pyrogallate for oxygen, and acid or ammoniacal solution of Cu_2Cl_2 for CO. The capillary is provided with a pinchcock, as in previous form. Being filled as the

figure indicates, the bulb, A, being the absorption bulb, is quite full, whilst the liquid rises in B only to the lower outlet. C contains the same liquid, but only partially filled. Hence the air has no access to the liquid in A and B, and can spoil only the liquid in C and D. When the gas enters A through the capillary, it pushes the absorption

FIG. 80.
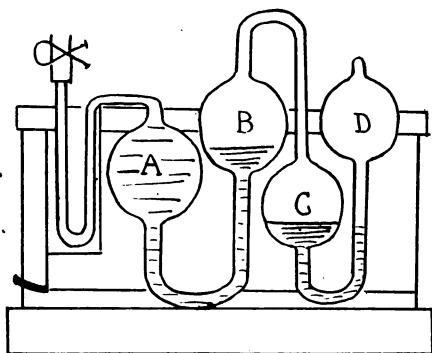
fluid into B, which is large enough to hold the entire volume of A. As the fluid rises in B, the nitrogen forces down the liquid in C until the bubbles can pass into D, and when, after the absorption, the gas leaves A returning to the burette, air will bubble from D into C. But it loses its oxygen to the liquid, and thus there is only nitrogen between the levels in B and C. In others words, C and D are simply *traps*.

The pipette, Fig. 81, serves when the absorption liquid attacks metal and yet a large wet surface is to be exposed to the gas; using, for instance, oil of vitriol

or bromine water. Here the bulb B is filled with glass beads.   These were put in by the glass blower before he narrowed the neck which unites B to A. Through the glass blower's dexterity we are thus in posses-sion of an elegant set of apparatus.   But suppose one of the pipettes meets with disaster just when

FIG. 81.
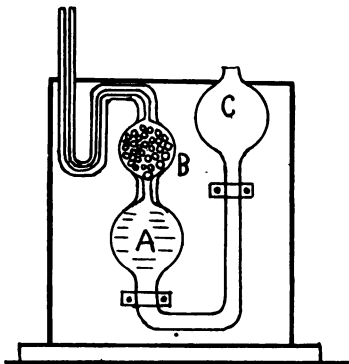
you need the set most. What then? A week would pass before you get a duplicate from the dealer.   Fig. 82 shows how an equivalent may be made quickly by means of 2 Erlenmeyer flasks, E, E'. The flasks should hold 200 c.c. each.   The flasks have doubly-perforated stoppers. Through one of the holes passes the siphon tube 1, $\frac{1}{8}''$ inside diameter, reaching to near the bottom of both flasks. Into the second hole of stopper E is stuck a piece of thermometer tube—there are always broken ther-mometers about a laboratory. The thermometer has a capillary canal, just what we need. The piece

is about $2\frac{1}{2}$ inches long; the sharp edges are rounded over a flame; the tube is stuck in so that the lower edge is flush with the stopper, avoiding any spaces for the lodging of gas. A piece of rubber tubing (black) $2''$ long is wired over the upper end and a pinch-cock clamped just above the end of the capillary tube. Through the second hole of stopper E' passes a short glass tube 3, $\frac{1}{8}''$ inside, to which a piece of rubber tubing 4 is attached (for convenience in blowing air). E may be filled with coils of iron wire gauze, or with glass beads to give absorb-

FIG. 82.
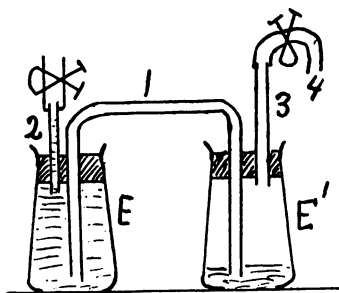
ing surface. In filling with absorption-liquid remove stoppers, pour into each flask so that the levels are even and nearly up to $\frac{1}{2}$ vol. of flask. Then insert stoppers very tightly, open pinch-cock and blow into rubber tube 4 until the liquid appears above the pinch-cock; then close the latter and E will remain full, ready to receive the gas. The two flasks form one unit. To prevent deterioration of stoppers, they should be coated with

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molten paraffin and after pressing them into the
necks, copper wire should be stretched across the
tops to prevent their slipping out, as the paraffin is
a splendid lubricator.   Such an apparatus gives
perfect results.   .If the measuring cylinder, the
burette, should break, you can construct a very
satisfactory substitute as follows : Make a square
block of wood 4″ side length and 3″ thick.   Bore
an inch hole clear through the center and a slot *S*,
Fig. 84, clear through the side, ¼″ wide.   Then nail

FIGS. 83, 84, 85.
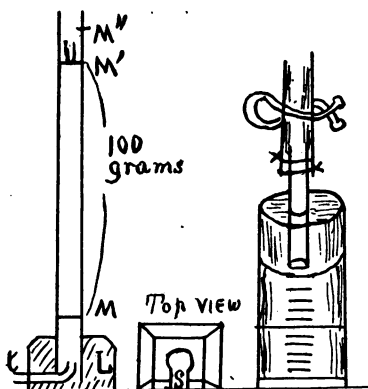
a square of heavy sheet lead (¼″ thick) across the
bottom as at *L*, Fig. 83.   The top edges of the block
should be bevelled.   This will give you an excellent
stand, or foot for the burette.   Select a piece of
glass tube as nearly cylindrical as possible of from
⅜″ to ¼″ inside dia. about three feet long.   Scrub
the inside of the tube with warm NaOH solution to

remove any fat; then rinse and dry. Round off
the sharp edges of one end, fit a cork or rubber
stopper with one hole, into which you have put a
$\frac{1}{4}''$ glass tube, bent as shown at t, Fig. 83. Close t
with a bit of wax plug; then set it into the foot,
after first sticking some cotton into the hole. Fill
with water to about 1 inch above the wood and
scratch with a file a line m at the upper rim of the
meniscus. Weigh into a beaker glass 100 grams of
water not nearer than 10 mgr. which is equal to
0.01 c.c. Pour this water into the tube. But re-
member that the beaker as well as the tube should
be moistened before either weighing or pouring, for
some water will adhere to the glass wall, thus caus-
ing an error.

Now make another scratch at the upper rim of
the meniscus m'. Now empty the tube and cut off
the latter $1''$ above m' at m'', round off the sharp
edges over the flame and fit a stopper into which
you have stuck $2''$ of thermometer tube, the edge of
the latter being flush with the under side of the
stopper. Fasten a strip of white writing paper
(several lengths may be stuck together) and lay off
upon it the distance m–m' accurately. Divide this
space into 100 equal parts, and each part into fifths.
Number every 10 c.c. and draw out in india
ink, cut it into a strip $\frac{1}{2}''$ wide, paste upon the tube
with a mixture of starch paste and liquid glue.
Remember that the wet paper expands and that the
two end marks will fall beyond the scratches on the
glass. In drying the contraction will bring the

paper back to the mark. When dry cover the back of the paper with molten paraffin, but not the glass. Press down the upper stopper so that its under face coincides with the zero mark m' as shown in figure ; the remainder of tube being already cut off. Now fasten the tube into the foot by pouring liquid wax into the narrow ring between glass and wood, the slot having been plugged with wood. Finally put 2″ of rubber tube upon the capillary and a pinch-cock. Thus the top of the burette will look as shown in Fig. 85. It is in every respect as good as a fully glass blown instrument, except that the scale is not apt to be quite as accurate, yet sufficient for all technical purposes. Never omit the wiring of the rubber, for if the rubber slips off the examination is lost. The analysis of our wood gas can now be proceeded with.

Note. All gases are more or less soluble in water. To avoid the error from this source completely the gas must be caught over mercury and measured over mercury—level glass and burette are filled with mercury. The error may be overcome partially, by saturating the water in the burette with the gas, *i. e.*, shaking the water with the gas, and the same with the absorbing liquids. The most soluble in water is CO_2, hence it is well to let water in burette saturate itself with CO_2, before the analysis.

To fill the burette with gas from the holder will be the first operation, taking advantageously just 100 c.c. to avoid figuring. In Fig 86 the arrangement of apparatus is shown in the moment of trans-

fer, when the gas has passed from *B* into the ab-
sorption bulb *A*, and the liquid from the latter into

FIG. 86.
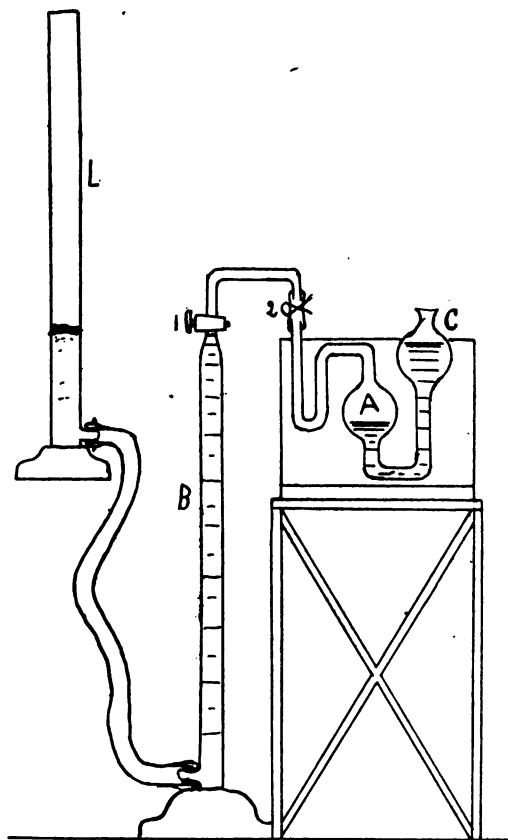
the tank bulb *C.* Stop-cock *1* and pinch-cock *2* are
now closed; the level cylinder dropped upon the

table. The operator seizes the frame of the pipette and the scaffold upon which the pipette stands, with both hands and shakes so that the liquid in A splashes all about the bulb and remains in contact with the gas; at the least for 5 minutes. Then open the cocks and the gas will flow back into B where the vol. is recorded.

The order in which the absorbents are applied is: (1) KOH for CO_2; (2) pyrogallate for O; (3) fuming sulfuric hydrate (oil of vitriol) for the heavy hydrocarbons; (4) cuprous chlorid in ammoniacal or in HCl solution for CO; (5) spongy metallic palladium for H.

In applying these to our gas, the gas from cellulose or wood, we find a shrinkage of volume after each application, except for oxygen. This element is only found when air has become mixed with the gas. The largest shrinkage is that due to hydrogen. After the absorption of H by palladium there is still a large volume of gas left. It must be, therefore, a gas which we have not met with before. We find it to be highly inflammable, and it burns with a pale, nearly colorless flame, if ignited at a platinum tip (for if the flame comes in contact with glass, the former is always of orange-yellow color from the sodium in the composition of the glass).

MARSH GAS, METHANE, METHYLHYDRID, CH_4.

When the gas in question burns we can easily demonstrate the forming of CO_2 and water, hence the gas must contain C and H, but might also contain O.

To get at the relative proportions of C + H we burn a measured volume within a closed vessel, so that none of the products can escape. Heretofore we used a simple eudiometer, the gas being above mercury. Hempel has constructed a pipette for this purpose. Fig. 87 shows this piece of apparatus. The bulb A is shaped into a neck or dome and thence is fused to the capillary. Into the neck two

FIG. 87.
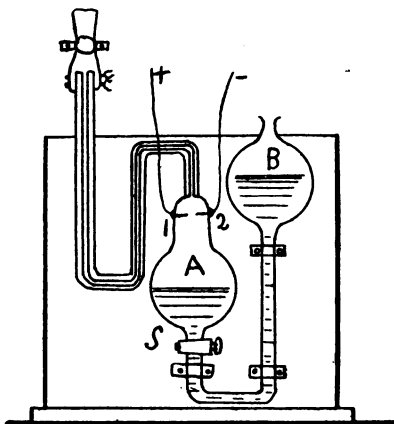
platinum wires are inserted by fusion, the same as in the eudiometer; these wires lead to the pole binders of an induction coil, thence to the battery. A being completely filled with water, we transfer from the burette, say 10 c.c. of gas, into A. We cannot use pure oxygen, because the explosion might easily shatter the relatively thin and weak bulb. We take air instead, thus diluting the effect of the

explosion by means of the inert nitrogen. 100
volumes of air contain 20.9 volumes O. As regards
the volume of air to be admitted we can reason
thus : If the total 10 c.c. were carbon gas then we
would need 20 c.c. of O, for 1 vol. of CO^2 contains
$\frac{1}{2}$ vol. C + 1 vol. O. If the whole 10 c.c. were
hydrogen, then we should need 5 c.c. of oxygen, a
total of 25 c.c. of oxygen or $\frac{25 \times 100}{21} = 119$ c.c. of
air. As both C and H are present, this volume of
air will surely give us an excess of oxygen. Let
this volume of air be transferred from the burette in
2 installments, then let the cock S be closed. The
expansion of the gases, consequent to the explosion,
will then throw itself upon the bit of rubber tube,
between the pinch-cock and the capillary, hence
the rubber tube must be very strongly wired upon
the glass, or the rubber will be surely flung off as a
bullet from a gun barrel ; the pinch-cock also must
be wired so that it cannot open under the pressure.
A screw clamp is, therefore, preferable to the spring
clamp. The rubber tube should be frequently re-
newed, as frequent expansion is apt to destroy the
elasticity of the rubber. Let the pipette be forcibly
shaken to effect a mixing of air and gas. Make
connection at commutator ; the spark is seen passing
between the platinum wires, but no explosion occurs ;
it should take place and mostly does take place.
When it does not occur the cause of failure lies in
too much dilution, the 10 c.c. of gas taken having
already much nitrogen admixed. Under these cir-

cumstances we generate in a voltameter *fulminating gas* (O + 2H), and let, say, 10 c.c. into *A*. Explosion is now certain ; the fulminating gas will act the same as the cap attached to the fuse, when a charge of dynamite is to be exploded. In our meaning the term explosion = instantaneous oxydation or combustion, or burning of C and H. A slower burning may be called a fire. The volume of fulminating gas need not to be measured accurately— because it simply disappears in the explosion as water, whose volume is trifling in comparison to the volume of the gas. After the explosion we open cock *S* and note a strong current setting from *B* into *A*, and this means disappearance of a certain portion of the gas. The disappeared portion we name the *contraction*, = *C'*, in this case 30.1 c.c. The volume of the gas mixture V, before the explosion was

V = G + A (G = gas 10 c.c. ; A = air 119 c.c.)

V = 10 + 119 = 129 c.c.

After the explosion

V′ = V — C′ (contraction) = 129 — 30.1 = 98.9

C′ itself is made up of H + O which disappeared as H_2O.

$$2C'/3 = H ; \quad C'/3 = O.$$

We pass the mixture into the KHO pipette and find a shrinkage of 9.8 c.c., which must represent the CO_2 formed from 10 c.c. of the gas. But 1 volume CO_2 contains 1 volume O, hence 9.8 c.c. of the 24.9 c.c. of O added went into the forming of CO_2 ; which

means that 10 c.c. of the gas contained 5 c.c. or $\frac{1}{2}$ *vol. carbon vapor.* We transfer the gas into the pyrogallate pipette and shake 10 minutes to absorb the remaining oxygen.

We find shrinkage = 5.1 c.c. oxygen; hence, deduct from total oxygen = 24.9 c.c.

<div style="text-align:center">

Consumed for CO_2 = 9.8 c.c.
Remaining oxygen = 5.1 c.c.
———
14.9

</div>

Therefore in contraction C′ enter 24.9 − 14.9 = *10 c.c. of O.* And as hydrogen = $\frac{2}{3}$C′; oxygen $\frac{1}{3}$C′; the *10 c.c. of O* correspond to *20 c.c. of hydrogen,* or if the original 10 c.c. of gas *be made = 1 vol.* it follows that 1 vol. of our unknown gas contains $\frac{1}{2}$ vol. C + 2 vols. H ; or 1 vol. C + 4 vols. H and its formula or symbolic expression is

<div style="text-align:center">

CH_4.

</div>

Here we have a body representing a compression of 2.5 : 1 ; 5 volumes of C + H compressed into 2 vols. CH_4. We have not had, therefore, a similar compound. Nevertheless the fact is proved by the specific gravity which is by calculation

<div style="text-align:center">

$\frac{1}{2}$ volume of carbon vapor = 0.4146
2 volumes of hydrogen   = 0.1382
———
0.5528

</div>

Several experimenters have found by independent methods, that is, both by weighing the gas, and by its velocity of diffusion, the number 0.5589 which is very close to the calculated figure. The name

marsh gas (*sumpf gas* in German) refers to the evolution of this same gas from swampy meadows where it sometimes gives rise to the peculiar phenomenon of the *will-of-the-wisp* (*irr-licht* = erring or wandering light), when by accident the gas becomes inflamed at one spot and the pale flame then setting fire to the adjacent bubbles thus produces the impression of a wandering or jumping flame, once thought to be *spirits*. In the summer months the gas always comes abundantly when the mud in swamp rivers is disturbed or poked into.

Marsh gas has neither odor nor taste. Mixed with air it causes no ill effects when breathed, is therefore not a poisonous gas such as CO, or a suffocating gas such as CO^2. 100 volumes of water absorb at 20° C., *i. e.*, the ordinary temperature of the air, 3.5 volumes of marsh gas.

When mixed with 8 to 10 volumes of air, or 2 volumes of oxygen, the gas explodes with great violence; but the temperature at which it ignites is higher than that at which hydrogen or hydrogen sulfid explode. These gases require only low red heat, while marsh gas requires yellow or white heat, showing that the elements $C + H$ cling very strongly together.

1 volume CH^4 + 3 or 4 vols. air does not explode; with 1 vol. CH^4 + 5½ to 6 vols. air the explosion is weak. And so again with 14 volumes of air, the explosion is weak; with still more air the CH^4 merely burns over the flame of a candle or lamp—no explosion. Now all this is knowledge of extreme importance to

the engineer who engages in coal-mining. For CH⁴ is
the gas which issues from the fissures of the coal beds;
and causes the fire danger in those mines, from its
life-destroying explosions.   The simplest instru-
ment for the detection of the danger; *i. e.*, the
presence of the marsh gas in the mine, breasts, stopes,
levels, was devised by Sir Humphrey Davy, eighty-
eight years ago.   He it was who first inquired into

Fig. 88.
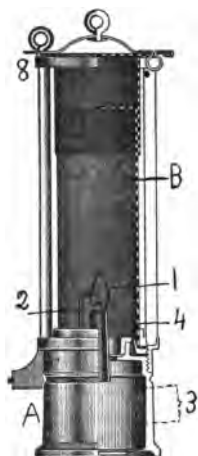
the nature of a flame and thus discovered a means
against the ignition of the inflammable mixture of
air and marsh gas.   Let *A*, Fig. 88, be the basin of
an ordinary oil lamp with a wick holder and wick
4; the oil level at *3*, the flame *1*.   *B* is fine mesh
wire cloth made into a truncated cone and the cone
is held by the brass ring *8*.   Thus no air can get to

the flame unless it pass through the gauze, and the product of the combustion must also pass through the gauze, since the top of the cone is closed by gauze. If the air contains CH^4 admixed, the flame begins to tremble, becomes longer and a bluish mantle forms around it. The whole interior may be filled with such a blue flame. This is due to the fact that with the deficiency of air the carbon only burns to CO and not to CO^2. But why does not the flame ignite the outside gas mixture? Simply because the wire gauze absorbs the heat so quickly that the temperature outside of it is too low to ignite the gas. The wick requires trimming from time to time and snuffing. These operations are performed with the wire 2, which passes through a stuffing box in the bottom of the lamp. The gauze must never be removed inside of the workings. Unfortunately the light given by such an affair is very weak and thus the men are tempted to remove the gauze and then comes the disaster.

Theoretical importance of marsh gas. CH^4 may be written

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$
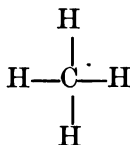
Four hydrogen chemical units evenly balancing the 4 affinity bonds of the carbon unit; in other words we say the marsh gas being a fully satisfied chemical complex, all other combinations of carbon

and hydrogen when saturated must be of the same type. Numerically we can express it $C^n H^{2n+2}$. When we found that paraffin showed the composition $C^{24}H^{50}$, we mean that we have here a compound built upon the *type* of marsh gas, yet while CH^4 equals a percentage composition of $75C + 25H$, the percentage in paraffin will be $85.3\,C + 14.7\,H$. All the members of the *marsh gas* or *paraffin series* have been found either as existing in natural bodies or they have been prepared by artificial splitting.

CH^4 = methane—marsh gas—a permanent gas.

C^2H^6 = ethane, a condensible gas.

C^3H^8 = propane, a light liquid.

C^4H^{10} = butane (in butter).

C^5H^{12} = pentane (five).

C^6H^{14} = hexane (six).

C^7H^{16} = heptane (seven).   Liquids contained in gasoline, benzine, and kersosene, also in tar.

C^8H^{18} = octane (eight).

C^9H^{20} = nonane (nine).

$C^{10}H^{22}$ = decane (ten).

$C^{24}H^{50}$ = paraffin ; a white, hard solid.

With the increase of C in the molecule, rise the specific gravity and the boiling-point. There are reasons for assuming in marsh gas the existence of a group (CH^3), in which there is still closer contact between the atoms than in CH^4. This latter becomes then the hydrogen compound of the form $(CH^3)H$. The group (CH^3) = methyl, is furthermore to be considered a *radical* or complex element, such as (NO^3), (SO^4) ; only with the difference that

this radical is of a positive or metallic character. It replaces hydrogen. Every elementary molecule is composed of at least two atoms. That is, hydrogen in the free state is not H but H^2; chlorine not Cl but Cl^2. Then in the hydrogen molecule H–H we can replace 1H by (CH^3) as its equivalent.

$$\binom{H}{H} + (CH^3) = \binom{(CH^3)}{H} + H = CH^4 + H.$$
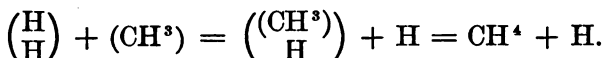
Or, again, $H^2(SO^4) + 2(CH^3)H = 2(CH^3).(SO^4) + 4H$; the latter compound is then methyl sulfate, same as sodium sulfate. In ethane C^2H^6, the older conception saw the radical ethyl C^2H^5 united to 1 hydrogen. But it is simpler to think of it as a coalescence of 2 methyl groups.

$$C^2H^6 = C^2H^5.H = CH^3.CH^3.$$

Propane, $C^3H^8 = (C^3H^7).H = propyl\ hydrid =$
$$CH^3.CH^2.CH^3.$$
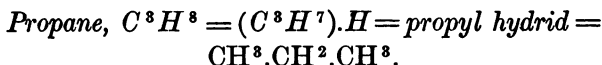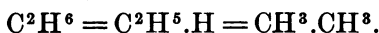
Two methyl groups joined by CH^2 which latter is the lowest member of the series C^nH^{2n}.

Butane, $C^4H^{10} = (C^4H^9)H = butyl\ hydrid.$ But on the methyl hypothesis there will be two combinations, which have been actually proved to exist, two bodies having exactly the same percentage composition, but distinct properties, to wit:

$CH^3.CH^2.CH^2.CH^3$, normal butane; and

$$CH{\underset{\diagdown CH^3}{\overset{\diagup CH^3}{-}}}CH^3,\ \text{iso-butane.}$$
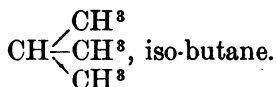
Such bodies as these, of equal atomic or percentage composition, are called *isomerids.* Isobutane is the *isomerdi* of butane.

For pentane C^5H^{12} there are three isomerids :

$CH^3.CH^2.CH^2.CH^2.CH^3$, normal pentane.

$$CH{\Large\langle}\begin{matrix}CH^3\\CH^3\\(CH^2.CH^3)\end{matrix}\text{ , di-methyl-ethyl-methane,}$$

and $\begin{matrix}CH^3\\CH^3\end{matrix}> C <\begin{matrix}CH^3\\CH^3\end{matrix}$, tetra-methyl-methane.

In the last we imagine a marsh gas molecule

$$\begin{matrix}H\\H\end{matrix}{\Large>}C{\Large<}\begin{matrix}H\\H\end{matrix}$$
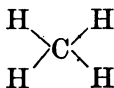
in which every hydrogen atom has become replaced or substituted by the methyl group. The second isomerid can be represented, to show the similarity, thus

$$\begin{matrix}H\cdot\\CH^3\end{matrix}{\Large>}C{\Large<}\begin{matrix}CH^3\\CH^2.CH^3\end{matrix}.$$
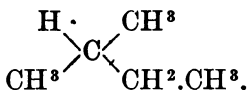
I beg to remind you that this so-called structural representation is not to mean a real picture—for in reality we have to deal with three dimensions, not with two as on this sheet of paper. This is an attempt to express symbolically the difference in properties of the *isomeric* bodies.

In the light of this exposition on marsh gas, we will reconsider the wood alcohol and the acetic acid. For the wood alcohol we had the atomic proportion CH^4O, it being then suggested that this formula may be written $CH^3(HO)$, and now we see that the methyl alcohol is a marsh gas in which 1 H is replaced by the radical (HO) hydroxyl.

$$\begin{matrix} H \\ \\ H \end{matrix} \Big\rangle C \Big\langle \begin{matrix} H \\ \\ (HO) \end{matrix}$$, methyl alcohol, hydroxyl methane.
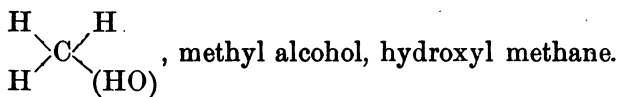
For acetic acid $H.C^2H^3O^2$ we can write

$$\begin{matrix} H \\ \\ H \end{matrix} \Big\rangle C \Big\langle \begin{matrix} H \\ \\ CO.OH \end{matrix}$$, acetic acid, hydroxyl-carbonyl methane.
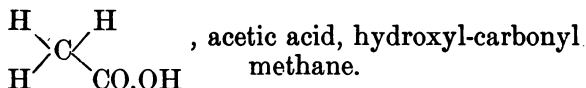
The group CO.OH, carbonyl-hydroxyl, is mono-valent; by the entering of this group into a hydro-carbon, the latter takes on the properties of an acid. The lowest form is *formic acid (ant acid)* $CHO^2.H$ which is found with the acetic acid. Here we can say that the group CO.OH is simply coupled with one H.

WOOD OR CELLULOSE UNDER PRESSURE AND HEAT.

If compressed cotton, or a stick of dry wood, or dry sawdust be enclosed in a strong glass tube as shown at Fig. 89, *A* in *figure 1*, and if the tube

FIG. 89.
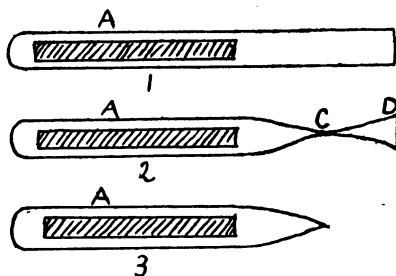
be then fused together as at *C, figure 2*, over a blast lamp and the part *D* be pulled off, the wood *A* will

20

be enclosed air-tight as in *figure 3*. Care must be had that the wall of the tube remains throughout of even thickness. If this tube be then placed within an air-bath, and the temperature be gradually raised to 320° C. as indicated by the air thermometer, Fig. 90, then it is evident that the distillation of the
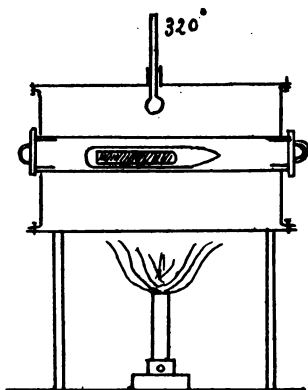
FIG. 90. FIG. 91.
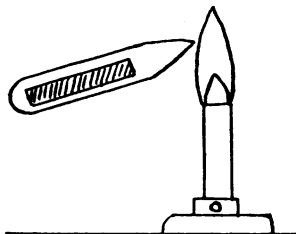
wood proceeds under increasing pressure : First, by the expansion of the air ; second, by the expansion of the gases and vapors which arise from the wood at this temperature. Let the condition of things remain thus for twenty-four hours. Let cool slowly. On examining the tube we find the wood converted into a jet-black shining mass; the cellulose structure is effaced altogether and the resemblance to *soft coal* is unmistakable. We open the tube very cautiously (after taking its weight) as follows : Since the pressure is still high (presumably) a sudden breaking

of the tube might have a very shattering effect (like a boiler explosion). Therefore, we approach the pointed end of the tube to a strong flame, as shown in Fig. 91. In measure as the glass nears red heat, it will become soft, and expand under the interior pressure until at the very tip it will be blown out, giving vent to the compressed gases. On weighing the tube, now, it is found that about 2 per cent. of the weight of the wood has disappeared, that much having been converted into permanent gas. Now we wash carefully the mass in the tube by means of alcohol (to dissolve any tar-stuff), and after drying in a current of dry air, find again a diminution in the weight of about 3 to 4 per cent. Altogether about 20 per cent. in weight of the cellulose has vanished. The importance of this experiment will appear in the next section.

CHAPTER XVI.

MINERAL COAL AND ITS CHEMISTRY.

WITHOUT mineral coal the industrial development of modern times would have been impossible. Some 250 millions of tons are now mined annually in the United States, much more than all the other minerals together. The conditions under which coal is found, and its association with other rocks, form a subject of *stratigraphic geology.* The points to which your attention is here called refer to the properties of coal and the uses to which coal can be and is applied owing to such properties.

We distinguish (*1*). *Hard coal or anthracite.* (Greek *anthras* = coal.) Color intensely black, luster more or less bright. Fracture smooth and spheroidal. Hardness considerable ; the pick does not produce much effect ; drilling and blasting is necessary.

(*2*). *Soft coal, bituminous coal, semi-bituminous, blacksmith coal.* Much softer than anthracite, color black, but color of fine powder is brown. Cleaves or breaks into prismatic pieces. When heated in glass tube gives off *dense yellow vapors* which separate into a liquid and into a combustible gas, whereas anthracite gives off *no vapors,* and only very little gas. If the coal melts into a black, thick liquid, it is called *bituminous (bitumen* being the Greek word for the

(308)

natural pitch also known as *asphaltum*).   If the coal merely softens in the heat, does not become quite liquid, then we call it *semi-bituminous,* (half pitchy).

(*3*). *Cannel coal,* has a black color but differs by absence of luster from the other varieties.   It breaks with an irregular surface.   When heated it does not melt nor become soft, but yields both condensible vapors and bright burning gas in abundance, (*cannel* is the Scotch of candle).   This coal is not as abundant as the other varieties and is of higher value, because it furnishes a larger volume of illuminating gas.   It is only used for gas-making.

(*4*). *Brown coal, lignite.*   Dark-brown color, dull in appearance, very soft, can be shoveled from the pit, shows the cell structure of wood and hence the name lignite (*lignum* = wood).   When heated it does not soften, but gives gas and tar, although less of these than cannel coal ; and more water.   It is usually mixed with sand and clay to a much larger extent than the other coals.   The beds lie near the surface, that is, they belong to more recent geological times.   Very abundant all over Western United States, Central Europe, Asia and Africa.   The cities of Northern Germany use this material exclusively for fuel, on account of its cheapness.

(*5*). *Peat, bog, turf.*   Brown or brown-black in color, very loose in structure and crumbly.   Acts like brown coal, when heated after having been dried.   This material is found always in flat regions, where the water cannot drain off and where no grasses can grow on account of the wetness.   But

on the other hand, the different varieties of mosses and algae develop and grow with astonishing rapidity, one generation on top of the other, each generation being very short-lived. Being so near the air the dead mosses undergo a partial rotting with the formation of marsh gas and carbon dioxyd. There are bogs known to be 50 feet thick and more. Ordinarily they do not exceed 3 feet in thickness. Yet they furnish to many localities their only fuel—Ireland, Holland, North Germany near the sea. The higher land of Western New York, where the Hudson, the Alleghany, and the Delaware rivers have their beginning, contains many peat bogs, which are more or less utilized. On the flat tops of very high mountains such bogs have been found. By a washing process the peat substance can be somewhat freed from the sand, and it can then be converted into cakes by pressing. Such cakes, when quite air-dry will give a hotter fire than wood, weight for weight.

Composition of coal. We find the ultimate or elementary composition by the same procedure which we followed with the cellulose. We burn a known weight, W, with copper oxyd and oxygen gas and collect the products of the combustion, conveniently for measuring or weighing. We find invariably the same elements to wit: Carbon, hydrogen, oxygen, nitrogen, sulfur. The two latter are *not* in cellulose, but they are found in other parts of plant structure. Nitrogen is *always* contained in the protoplasm, and sulfur sometimes; without the protoplasm no plant can develop—it is the blood of plant

life.   The seeds of plants always contain much nitrogen (15 to 17 per cent.).   Coal contains from 1 to 3 per cent. of nitrogen.   The sulfur varies between wider limits.   The sulfur can be in *union* with the carbon and the hydrogen, and is then *invisible;* or combined with iron as yellow pyrite, and is then readily visible.

Coal always leaves a residue after the carbon and hydrogen have been volatilized by oxidation into CO_2 and H_2O.   The residue is called *ashes,* because wood leaves ashes.   The two kinds of ashes are very unlike.   From coal ashes water does not extract potash, nor any other body; coal ashes are quite insoluble; no alkaline reaction whatever. Neither HCl nor HNO_3 nor H_2SO_4 dissolve it, only HF.   The ashes in fact contain chiefly the oxyds of silicon and aluminum SiO_2, Al_2O_3, and Fe_2O_3 when the ashes have a brown color.   The clinkering or semi-fusion of the coal ashes is due to Fe_2O_3 which acts as a flux upon the other oxyds; white coal ashes never show clinkering.   The following analysis, made by me lately, gives the ultimate composition of a soft coal from Kansas.   Carbon = 75.35, hydrogen = 5.50, oxygen and nitrogen = 10.10, sulfur = 1.54, SiO_2 = 4.35, Al_2O_3 = 2.70 (being together ashes equal 7.05, snow white) moisture = 0.45.

Notice the total absence of iron oxyd, whence it follows that the sulfur must be combined with the carbon and hydrogen.   This coal belongs to the semi-bituminous variety verging upon cannel; for

the residue merely adheres slightly after having been exposed to a high yellow heat, and like cannel it has a dull, black color; powder brown.

The *proximate composition* of the different varieties is but imperfectly known, or rather guessed at. I mean by proximate composition the molecular structure—the manner of combination of the elements. You can do no better than to imagine the coal to be an intimate mixture of solid hydrocarbons, oxy-hydrocarbons, sulfo-hydrocarbons, nitro-hydrocarbons, amorphous carbon, and mineral particles constituting the ash. The different varieties of hard and soft coal arise from the preponderance of one or more of the above groups of molecules. Reasons for this hypothesis are: (1) The crystalline structure of the coal, revealed in thin translucent plates or sections under the microscope; (2) The actions of solvents upon the coal, such as ether, benzole, carbon disulfid, potassium or sodium hydroxyds.

Origin of coals. That cellulose is the original material there is no reason to doubt; all hypotheses or theories start with this base. Generally, however, geologists assume that the material for the coal beds consists in the successive growth of tropical forests one on top of the other. My own theory differs from this. The chief reasons are that in many places we find trees standing upright in the coal beds, reaching even into the sandstone or slate strata lying over the coal bed as shown in Fig. 92. Here a section is reproduced from an English coal

mine.   *a* is limestone, *b* is fire-clay (under clay), *cc* the lower and upper benches of a coal seam, *e* black coal slate, *f* sandstone, *g* brown slate.   *ttt* are fossil trees, whose bark is also coal, but whose interior is sandstone, because these trees belonged to the class of giant reeds, *calamites lepidodendron, sigillaria, etc.*, and therefore contained a pithy interior and a very strong fibrous rind, very resisting to chemical change.   *d* is a band of slate separating the coal-

Fig. 92.
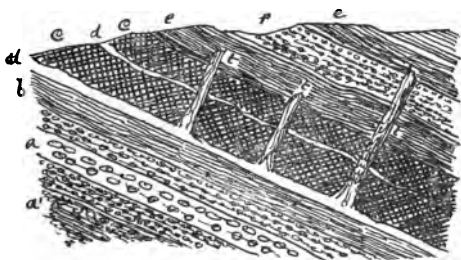
bed into the two benches.   The strata *a* and *b* were in horizontal position during the coal-forming times and the conditions of level equal to that of very shallow basins very near the sea level ; that is, the general conditions were those of a tropical swamp as we find them in our time along the Amazon River in South America.   At first these conditions were favorable to the growth of the great ferns and the gigantic reeds.   Later on, the land sinking very slowly, the swamp became too wet for this vegetation and in its stead algae—the lowest type of plant life—which you find always in the shallow pools of

our present swamp woods, the green and brown threads began to flourish abundantly, luxuriantly. An alga is a plant consisting of one cell or of an aggregate of cells, of which however each cell remains a life unit. Each cell has a thin wall of cellulose enclosing a liquid interior in which there is a floating patch of protoplasm, the cell-nucleus or cell-kernel. While these generations of very rapidly growing cells died and accumulated on the bottom of the pool, or rather upon their dead predecessors, and being under water could not *rot*, the rivers or creeks emptying from higher ground into the swamps brought the fine sand and clay which settles very slowly, as you well know from the rivers remaining turbid long after a freshet. In time this material—the *silt*—settles and mixes with the vegetable ooze, and there we have an explanation of the intimate admixture of the ash particles with the coal, and also an explanation of the strong variation of the ash percentage in the different parts of a coal bed. Whenever a slate band occurs in the coal, according to this theory, we presume that an unusual freshet carried the silt faster into the basin than the algae could accumulate, in fact the muddiness interfering with rapid growth. The silt also settled into the hollow trunks of the trees, thus preserving them against collapse by external pressure.

My theory of the algae accounts also for the high percentage of nitrogen, which we find in the coal, because the relative percentage of protoplasm to cellulose or of nitrogenous substance, is larger in

the algae than in the complex cell-structures of trees. During the accumulation of the ooze a decomposition of the dead algae cells began to set in, alike to that which we now-a-days observe in the peat bogs, by which the percentage of carbon in the residue steadily increases, while hydrogen and oxygen, notably the latter, decrease: CO_2 forming and CH_4 and H_2O. At last, the ground sinking more rapidly, the influx of silt increases and the vegetation stops, the sea finally encroaches upon the swamp and the materials for sandstone or limestone are brought in. They cause a steadily increasing pressure, under the influence of which internal heat arises, which cannot dissipate as the rocks are very bad conductors of heat. Thus the plant material comes gradually under the conditions of the experiment upon cellulose, described a few pages back. Wherever the pressure was greatest the change towards *carbon* was greatest. Thus we find in Eastern Pennsylvania only anthracite with 90–94 per cent. of carbon, because the side pressure upon the strata was so great, that the latter became greatly bent and even doubled upon themselves as shown in Fig. 93, whilst in the Western States the strata remained in their original horizontal position, as seen in Fig. 94, except in Colorado, and hence we find anthracite in the latter state. The dotted lines in Fig. 93 denote that part of the coal bed which has been removed and lost by surface destruction and the forming of the present topographical outlines. All the details of the structure of the coal

measures belong to geology; only sufficient had to

FIG. 93.
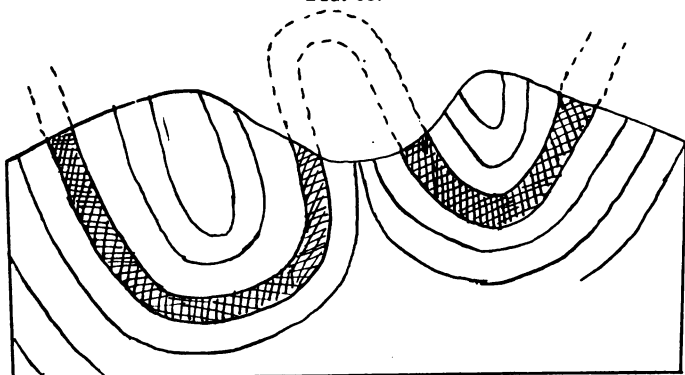
FIG. 94.
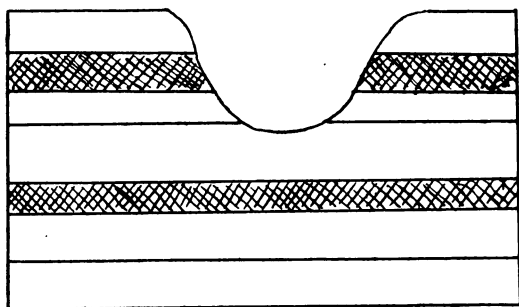
be introduced here to make the chemical theory intelligible.

DISTILLATION OF COAL—COKING PROCESS.

By distillation of cellulose—or wood—we obtained charcoal, tar, pyroligneous acid, CO, CO_2, CH_4, H; and since coal is derived from cellulose

we may and should expect similar, if not identical, products. In order to test this proposition we rig up the set of apparatus, Fig. 76, page 275. The tube T we charge with the coarsely-powdered coal, so that when the tube lies in horizontal position and has been tapped upon, the coal only fills one-half of the tube. Why? Because at red heat the bituminous and semi-bituminous coals swell up, thus clogging the tube to the escaping gas, which latter, with increasing pressure, will invariably break the tube. We start heating at the front by using the diaphragm or shield S. First we note a heavy yellow vapor, from this condenses a brown liquid in the receiver $\mathcal{S}$, and the bell B fills itself with gas. The first portion of gas we allow to escape, because it is mixed with the air in T and $\mathcal{S}$. Anthracite gives no vapor, no condensing tar, only a relatively small volume of gas; because anthracite has already undergone the distillation under the influence of great pressure. When, at bright red heat, the evolution of gas becomes very slow, or stops altogether, we disconnect the receiver $\mathcal{S}$ from T and B from $\mathcal{S}$. We pull the tube T from the furnace, let it become cool, and then break the tube. We find the residue more or less bright, porous, dark or light grey in color. With large pores the stuff is more or less friable, with small pores it becomes hard and tough. For bituminous and semi-bituminous coals the weight of the residue is from 50 to 65 per cent. of the original weight of the coal. The technical name of this residue is *coke*, which

word is derived from to cook, and may have been merely a provincial substitute for cake. When brought up to a red heat in a current of air the coke burns *without* making a visible flame, although it still contains a remnant of hydrogen and oxygen, for the complete change of coal to carbon depends upon the temperature and time. At a white heat (in fire-clay crucible), the last remnant of hydrogen can be eliminated. The ordinary coke is, therefore, a mixture of the ashes with carbon (amorphous and also graphitic), and more or less hydrocarbon.

Coke is required as fuel in blast furnace work, especially in the high-stack-furnaces for the reduction of iron ores. Why? Because if coal were used, the latter would convert itself into coke in the furnace, would cause a *loss* of heat energy (elimination and decomposition of the hydrocarbons and oxy-hydrocarbons requires heat addition from outside sources), and the coke thus forming would cement the pieces of ore and flux into a solid cake, through which the large quantities of nitrogen and carbon monoxyd are blown in at the bottom of the furnace could not pass—the furnace would clog or choke and eventually extinguish itself.

For this need of the blast furnaces, immense quantities of coal are converted into coke. The apparatus for making coke is known as coke oven, not kiln or furnace, but *oven*. Why? Because the first coke was made in Dutch bake-ovens. The so-called *bee-hive* coke oven of the present time is merely a slightly modified bake-oven. In this oven all the gas and

the tar are wasted. In the scientifically constructed ovens, the gas and tar are utilized. Different ovens have been constructed in Europe in great profusion. Those mostly used now are the Solvay oven, and the Hoffman oven; they have also been introduced into the United States. The detail of coke-making belongs to *metallurgy*. We turn now to the contents of the receiver (3). As in the distillation of wood we find two liquids, one oily the so-called coal tar, one watery of light-brown color. This watery liquid smells of *ammonia*, and turns red litmus paper blue. Thus it is the reverse of pyroligneous acid from wood distillation. Addition of acid to the ammonia water produces effervescence: CO_2, H_2S are given off, hence the water contains ammonium carbonate and ammonium sulfid. The occurrence of the ammonia proves the presence of nitrogen in the coal. The absence of the acetic acid may be explained from the smaller percentage of oxygen in the coal and from the higher temperature needed to break up the coal, a temperature at which $C_2H_3O_2.H$ breaks up into $CH_4 + CO_2$. The principal market for ammonia being that as *fertilizer*, the cheapest way of extracting the former is to convert it into *sulfate*. The water is neutralized with H_2SO_4 and the solution evaporated by means of the waste heat from the ovens. The result is dark-brown, crude sulfate. This is redissolved in the requisite quantity of boiling water, filtered through a bed of charcoal to remove the tar which separates during evaporation, and the liquid is run

into flat basins, where the sulfate crystallizes on cooling. This second product is still yellowish, but good enough for the market.

The coal tar, the oily portion of the condensed vapors, is composed essentially like the wood-tar. But certain valuable hydrocarbons are contained in the coal tar in larger percentage. These hydrocarbons are: benzol (C^6H^6), toluol (C^7H^8), phenol ($C^6H^5(OH)$), naphthaline ($C^{10}H^8$), anthracene ($C^{14}H^{10}$). When the tar is subjected to distillation, light oils pass over first up to a temperature of 180° C. Benzol, toluol, phenol are contained in this portion; at a higher temperature oil passes over which solidifies on cooling. The cooled mass can be recrystallized from an alcohol solution, or it may be purified by sublimation. In this purified state it forms large thin crystals in form of plates with the luster of mother of pearl and a strong peculiar odor. This is the *napthaline* of trade and is largely used to protect woolen and fur goods against insects: *moth-balls*. Only the oil which passes over between 80° and 100° C. is used for the manufacture of benzol. Between 100° and 130° C. toluol and phenol with some benzol pass over. Pure benzol is a colorless very mobile liquid; boils at 82° C. and crystallizes at 0° C. Specific gravity = 0.85.

Nitrobenzol, $C^6H^5.NO^2$. Is obtained by treating the benzol with a mixture of conc. H^2SO^4 and very conc. or fuming HNO^3 in cast-iron cylinders, which can be cooled by running water, because the reaction is very energetic; 1 hydrogen of the C^6H^6 is removed as water and nitrobenzol results.

$$C^6H^6 + HNO^3 = C^6H^5NO^2 + H^2O.$$
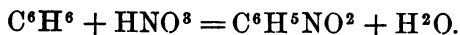
Nitrobenzol is a yellowish heavy oil which boils at 205° C.; and has a pleasant odor resembling that of the oil made from bitter almonds. If an excess of HNO^3 is used the dinitrobenzol $C^6H^4(NO^2)^2$ results.

Anilin, C^6H^7N. A small quantity of this highly interesting substance is already contained in the tar. But from nitrobenzol it can be obtained in any desired quantity. Anilin forms a colorless liquid, diffracts light strongly, has a peculiar odor and burning taste. The oil boils at 182° C. and solidification sets in at 8° C. Specific gravity = 1.02. Is very slightly soluble in cold water, more so in boiling water, but quite soluble in alcohol, ether, carbon disulfid, and coal oil. It burns with a very smoky flame. Is very poisonous. Chemically anilin may be considered as ammonia in which 1 H has been replaced by the hydrocarbon radical *phenyl* thus

$$\left.\begin{array}{c} H \\ H \\ H \end{array}\right\}N = \text{ammonia.} \qquad \left.\begin{array}{c} (C^6H^5) \\ H \\ H \end{array}\right\}N = \text{anilin.}$$
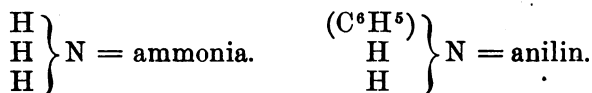
Like ammonia it unites with HCl and other acids and forms salts: $C^6H^5.H.HNHCl =$ anilin chlorid. These salts are mostly easily soluble in alcohol and crystallize readily. Anilin is a fine example of a *complex base.*

Methylanilin is another base, arising from a second hydrogen being replaced by methyl, thus:

$$C^6H^5.H.H.N + CH^3I + \text{heat} = (C^6H^5)(CH^3).H.N + HI.$$

21
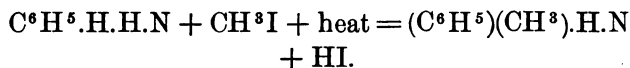
This body, known as "Mauve de Paris," colors silk and wool a fine violet color.

Rosanilin, fuchsin. This was the first splendid dye-stuff prepared from coal-tar through the way of anilin, by means of oxydation ; usually As^2O^5 is used as the oxydizing agent. 100 parts of anilin oil are poured slowly into 150 parts of a water-solution holding 75 per cent. As^2O^5 in an iron vessel with stirring apparatus. The temperature is raised and kept for five hours at 182° C. Water and unchanged anilin dissolve during this period. The semi-fluid residue has a bronze color, and from it the dye-stuff is extracted by boiling water, filtered, under pressure, through felt. Solution contains the rosanilin as arseniate and the As^2O^3 which is formed during the process of oxydation. By saturating the solution with NaCl (equal in weight to the residue), the hydrochlorid of rosanilin forms and Na^2HAsO^4. *Red crystals* fall out, in measure, as the liquid cools. By recrystallizing this first product a higher grade is obtained. The red crystals, being the chlorid of rosanilin, are known in the dye-works as *fuchsin.* By acting on the water solution with NaOH, the base *rosanilin* is obtained as a white precipitate, which becomes intensely red in contact with any acid. The composition of *rosanilin* is $C^{20}H^{19}N^3$. It forms thus :

$$2 \begin{array}{c} C^7H^7 \\ H \\ H \end{array} \middle| \begin{array}{c} \\ N + \end{array} \begin{array}{c} C^6H^5 \\ H \\ H \end{array} \middle| \begin{array}{c} \\ N+3O = \end{array} \begin{array}{c} C^6H^5 \\ C^7H^7 \\ C^7H^7 \end{array} \middle| \begin{array}{c} \\ N^3+3H^2O. \end{array}$$
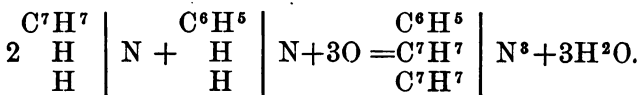
The 3O are furnished by As^2O^5 or any other oxy-

dizing agent.   But we see that another body is here contained, the *toluidin*, besides the anilin.   Remembering, however, that the raw oil contains benzol and toluol, the phenomenon is explained.

The crystals of fuchsin are green-golden in appearance, like a brilliant metal.   They dissolve in water with intense red color.   If well cleansed silk or wool be hung in such a solution, the liquid becomes colorless by degrees, all the coloring fuchsin will have transferred itself to the fibre, producing thereon the beautiful red tints according to the quantity transferred.   The color fixes itself, does not require a *mordant* or fixing agent.

Mauvanilin, $(C^6H^5)(C^6H^5)(C^7H^7)N^3.HCl$ gives an orange-yellow dye.   A great many other beautiful dye-stuffs have been produced by further substitution of hydrogen in the base by other radicals, as anilin, toluidin, or simply methyl, ethyl, and others. My main purpose in devoting so much space to this subject was to impress upon you the possibilities lying hidden in such a material as the ugly, bad-smelling coal-tar, and the great fortunes which have been made by utilizing it in the right way.

CHAPTER XVII.

THE GASES FROM THE DISTILLATION OF COAL— MANUFACTURE OF ILLUMINATING GAS AND GAS COKE.

The contents of the bell jar are at first cloudy from exceedingly small particles of semiliquid bodies, which will condense after a time, forming a thin layer of tar upon the retaining water surface. If now the gases be subjected to the analysis by absorption which has been given in detail under cellulose or wood, it will be found that the composition by quality does not differ much ; the relative quantities differ considerably, and even very much when the gas from the early distillation is compared with that which is given off at the end of the operation. We find H, CH^4, CO, CO^2, non luminous: C^2H^4, C^3H^6, C^4H^8 and C^2H^2, (acetylene) as luminous gases. NH^3, SH^2, CS^2, CN as impurities.

Of the luminous or light-producing hydrocarbons *ethylene* (C^2H^4) olefiant gas (oil-making gas) is the most important; of propylene (C^3H) there is least ; of butylene C^4H^8 there is usually from $\frac{1}{2}$ to $\frac{1}{3}$ as much as of ethylene. These hydrocarbons combine with chlorine, bromine or iodine, thus :

$C^2H^4 + 2Cl = C^2H^4Cl^2$, *ethylene chlorid* an oil-like liquid (hence the name olefiant or oil-making.) Spec. Gr. $= 1.174$.

(324)

At red heat ethylene breaks up, thus:

$$C^2H^4 + \text{red heat} = C + CH^4, \text{ amorphous carbon}$$
$$+ \text{ marsh gas.}$$
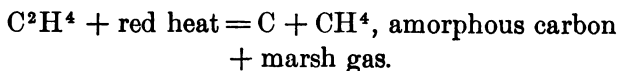
It is this action which we call *dissociation*, that accounts for the smoking of a gas flame.   If oxygen is present both C and CH^4 are oxydized to $2CO^2 + 2H^2O$.   Bromine acts like chlorine upon ethylene: $C^2H^4 + 2Br = C^2H^4Br^2$ an oily liquid as the preceding one.   Propylene and butylene are acted upon similarly: $C^3H^6 + 2Cl = C^3H^6Cl^2$; $C^4H^8 + 2Cl = C^4H^8Cl^2$, propylene chlorid, butylene chlorid. Hence it follows that we can remove these three gases from a mixture of gases by shaking the mixture with bromine water in a suitable gas pipette. The higher we find their percentage in a given gas the more we are sure of a bright light, provided that the burner be suitably constructed.

PLAN FOR GAS WORKS.

Figs. 95 and 95a give the essential pieces of apparatus for the production of illuminating gas by distillation of coal, in ground plan and length elevation. R, R', R^2 represent a fire-brick retort and ovens for heating them to a yellow heat. H is a sheet-iron pipe 18″ to 24″ in diameter and known as the " hydraulic main."   The elevation shows how the retort connects by a goose-neck pipe with this main and also that the pipe dips under the water level of the main, thus producing a light pressure upon the gas in the retort.   Most of the condensible constituents of the gas become liquid in contact with the liquid in the

Fig. 95.
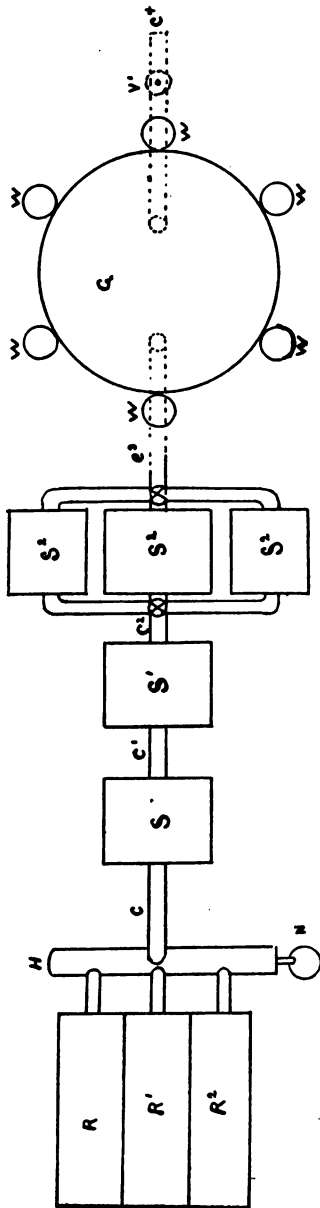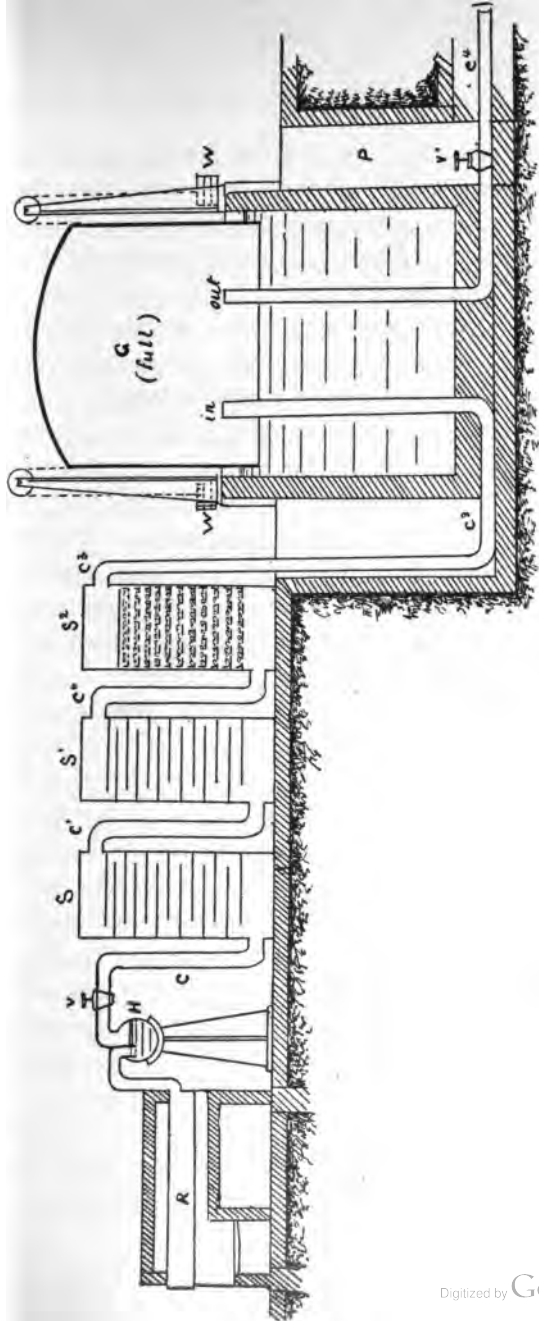
pipes. At N there is provided an overflow which drains into a vertical tank or cistern; thus the level remains always the same in the main. Steam, tar, ammonium salts are condensed largely. A pipe C leads from top of main to the purifying towers S, S', S^2 which are technically known as *scrubbers*. S, S' are *wet* scrubbers, because the gas must pass the extensive surface of the horizontal trays over which flows a film of cold water. All the ammonium compounds and all the tar are removed from the gas in these wet scrubbers, but the gas still contains a notable quantity of hydrogen sulfid. The latter is taken care of in S^2 which is a *dry* scrubber, for here the trays are covered each with a layer of *Laming's mass*, to wit: a mixture of $Ca(HO)^2$ with $FeSO^4 + 7H^2O$ (copperas). $Ca(HO)^2 + FeSO^4 = CaSO^4 + Fe(HO)^2$; it is the latter, ferrous hydroxyd, which is the active agent. At first $Ca(HO)^2$ (dry slaked lime) was used alone. $Ca(HO)^2 + H^2S = CaS + 2H^2O$. But the action is slow. When the book-backs in the public libraries of London and other cities began to crumble away, the cause was traced to the gas flames and more specially to the sulfuric oxyd produced by them, *i. e.*, by the burning of H^2S to SO^3. Then Laming invented the mixture and thus checked the evil, without knocking it out altogether. The carbon disulfid CS^2 has, so far, resisted all attempts at absorption in the scrubbers. The dry scrubbers must be provided in duplicate or triplicate, because they need frequent renewing of the Laming mixture, which becomes

foul as the men say.   The gas is now ready to flow through the pipe C'' into the holder G.   The holder is a sheet-iron tank of circular or cylindrical shape.   It is closed at the upper end and dips with the open lower end into water of the walled and cemented cistern C.   The tank G is held in place by 6 or more guide rolls, and is counterbalanced by the 6 weights W, W, etc.   These consist of cast iron disks, superposed, so that the bell may be made to press upon the gas at any pressure, by adding or removing a disk, from each or to each, of the 6 weights.   By adding disks the bell may take the function of a suction pump thus causing the gas to overcome the friction of scrubbers, during the progress of the distillation.   The elevation explains the entrance of the gas at *in* and the outflow at *out* if the main valve V' is open.   This valve is always accessible through the pit P.   The dimensions of the plant follow from the rate of consumption of the gas.   As one 15 candle-power burner consumes 5 cubic feet of gas per hour, and as the burners are needed on the darkest day for 8 hours, and as each family uses on the average 4 burners, we get 160 cubic feet per family per day.   1000 families require 160,000 cubic feet + 10 per cent. for street lighting, total 176,000 cubic feet, hence 18 tons of coal will be required per day giving roughly 9 tons of coke. A bell 30 feet in diameter and 20 feet high will hold 16,000 cubic feet.   Ten such would be required to store the 160,000 cubic feet.   However the bell serves more as a regulator than as a storage.   The

retorts are kept going all through the hours of largest consumption. One holder is sufficient for each 1000 families. Holders of 100 feet diameter and 25 feet high have been built in large cities. The retorts are made of fire-brick material and have a $\frown$ section. They are 5 to 6 feet long, 18 to 24 in. wide (inside), 12 to 15 inches high. Thickness of bottom 3 to 4 inches, of sides and top $2\frac{1}{2}$ to 3 inches. The average daily capacity per retort is 5000 cu. feet; hence 32 retorts will be required for 160,000 cu. ft. daily production. The retorts are best arranged in batteries of 7 each with one common fire-place.

WATER—GAS.

(a) *Water-Gas.* $H_2O + C = H_2 + CO$ at yellow or white heat. The mixture of hydrogen and carbon monoxyd burns with colorless flame, hence the gas must be made luminous by the addition of gasoline or hydrocarbons of the olefine series. Prof. Lowe of Norristown, Pa., introduced the application of this reaction into the gas industry about 1873. It displaces the distillation process, but has not been introduced in many gas works until more recently in a modified form.

The action $H_2O + C = CO + H_2$ is *endothermic,* heat-consuming.

The action $C + 2O = CO_2$ is *exothermic,* heat-producing.

Hence the process of preparing water-gas is necessarily a double one. Let *1, 2,* Fig. 96, be two

fire-brick cylinders held each in a sheet-steel mantle. Let these cylinders stand upon iron pillars, *10, 10, 10*, which will enable a dropping of the hinged bottoms, *3, 3*, and thus an emptying of the cylinders of ashes and klinkers. Let the cylinders be filled with pieces of coke or charcoal. At *4, 4* we have charging hoppers. At *5, 5* air-pipes enter the cylinder, and at *6, 6*, steam-pipes. At *7, 7* small

Fig. 96.
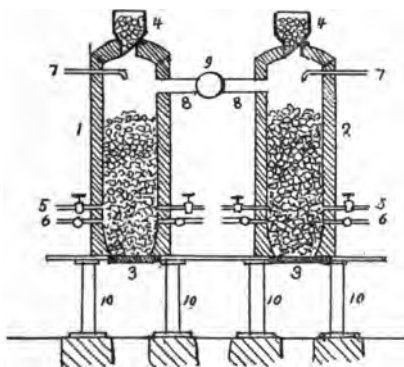
pipes can introduce coal-tar. The gas passes at *8, 8* into the common pipe *9*. Before charging the coke, small wood and shavings are put into the cylinders to start the fire with in one cylinder first. Then compressed air is allowed to enter the through pipe *5*, coke is charged until it reaches just below the gas outlet *8*, and the valve in the hopper *4*, is left open. Under these conditions, a gas mixture passes out from the hopper, which is composed of nitrogen, chiefly

(60 per cent. to 70 per cent.), carbon dioxide and carbon monoxyd ($N + CO_2 + CO$). The sum of $N + CO_2$ being at the least 75 per cent., it follows that this gas is only a low-grade heat-producer, and is therefore allowed to escape through the hopper. When the top layer of coke has come to bright red heat, the lower layers will be at white heat. The hopper valve is now closed, and the valve at *8* opened. The air valve in *5* is closed, and the steam valve in *6* opened. As the steam impinges upon the white-hot coke, it breaks up into $H_2 + CO$. If the valve in the tar pipe *T* be now opened properly, the tar will fall upon the bright red coke and be *dissociated*, i. e., the higher molecules of C_nH_n, C_nH_{2n} and C_nH_{2n+2} will be broken up into the lower members of the series, into carbon and into marsh-gas. Read again what is said about this under tar and the distillation of coal. All these hydrocarbons will mix with the main mass of hydrogen plus carbon monoxyd, will pass through pipe *9* into the gas holder, or directly to the burners, and yield a fine light, or if more air be allowed to mix with the gas in the burner, a very intense heat, and a non-luminous flame. All this while the white heat of the coke drops down steadily to a red heat and H_2O can be no longer decomposed. In common language we say that the steam quenches the fire, i. e., extinguishes it. But the second cylinder has been brought up to white heat during the time. We shut off the first cylinder from pipe *9*, open the valve *8* and the steam valve, repeating

all the operations as before, while the first cylinder
is again blown to white heat—exchanging the
steam for air. Thus by means of the two cylinders
a perfectly steady stream of water-gas is produced.
A battery of three cylinders is more advantageous
still, for then we can throw out one after another
of the cylinders for the purpose of removing the
ashes and klinkers without danger of explosion.

FUEL—GAS.

Under this name goes a mixture of gases of in-
ferior grade to the water-gas; cheaper correspond-
ingly, and much in use, at this time, in metallurgi-
cal works and also for the feeding of *gas-engines*.

FIG. 97.
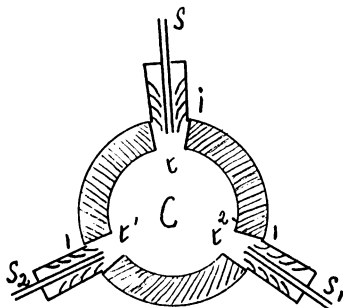
Chemistry. Steam and air are blown into the
coke simultaneously; the air and the steam periods
of the water-gas process are thrown into *one* period.
One cylinder only is required for the same volume
of gas per minute. Let Fig. 97 represent the sec-

tion plan of the cylinder in the level of the steam pipe 6, Fig. 96; let S, S_1, S_2 be the three steam pipes and i, i, i the parabolic injectors (system of Koerting). Then there will be sucked up by the steam jets a volume of air depending upon the velocity of the steam (pressure) and upon the capacity of the injector. The pressure of the steam must be adjusted to the capacity of the injector so that the exothermic product $CO^2 + N^4$ is larger by about $\frac{1}{5}$ than the endothermic product $C + H^2O(CO + H^2)$. The $\frac{1}{5}$ over energy is consumed by loss of heat through conduction, radiation and fusion of the ashes. The latter, the fusion of the ashes, can not be obtained unless a proper amount of CaO be charged with the coal or coke and the percentage of

Fig. 98.
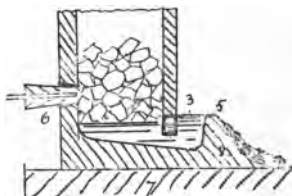
each as well as the composition be known. A lip or outflow must be provided for the slag as shown in Fig. 98, where 1 is the slanting bottom, 2 the dam of the forehearth, 3 a hollow iron beam, through which water circulates to keep open the outflow and prevent the eating away of the firebrick; 4 is the inner level of the liquid slag; 5 is its outer level and when more slag comes it will run over the

dam ; *6* is the twyer or opening for the injector ; *7* is the foundation. If raw soft coal is to be used in this fuel-gas proposition, the cylinder must be provided with a rotating breaker, to prevent the forming of cakes and lumps, which always make poor gas.

PETROLEUM, ROCK-OIL, MINERAL OIL.

The term *coal-oil* is most used in the United States. It is not a good name because implying a relationship between coal and this oil. Such a relationship has not been proven in any instance. All the Pennsylvania, Ohio, West Virginia, Indiana oil comes from rocks which lie under the coal measures, very much older in order of formation. *Rock-oil* is a perfectly appropriate term. In regard to the origin of the oil in these rocks, the most plausible opinion is that of Engler who ascribes the oil to enormous numbers of dead fish within the sand, which now forms the oil-carrying strata. Engler obtained oils very similar to coal-oil by subjecting fish to great pressure at temperatures not much above the boiling-point of water.

Finding of the oil. Along Oil Creek, Pa., the oil was found but 50 feet under the surface, but for the most part the oil strata are buried deeply. The gushing or flowing of the oil from a fresh hole is due to the accumulated pressure of marsh gas. As this pressure becomes released the automatic flowing ceases, and pumping becomes necessary.

Physical properties of the oil. Most oils are colored ; they appear red or brown-red in transmitted

light and opalescent green in reflected light. This double-color or *dichroism* is owing to the presence in the oil of one constituent which has received the proper name: *fluorescin*. The odor is very strong and characteristic. Sometimes the crude oil is quite mobile and sometimes it is thickish, viscous. So also varies the specific gravity from 0.75—0.95. None has yet been found heavier than water. The crude oil is usually quite inflammable.

Chemical properties. In general it will hold true to say: Petroleum is a *complex* liquid. The constituting members of the complex are hydrocarbons of the marsh gas or paraffin series (C^nH^{2n+2}). The individual members of the series can be separated by fractional distillation many times repeated (see under wood-tar and coal-tar). The members from C^4H^{10} to $C^{16}H^{34}$ have actually been prepared by several chemists. The density of the liquid and its boiling-point are the mean of those constants proportionately to the percentages of the constituting hydrocarbons. The heat-value of coal-oil is very high, much higher than that of vegetable and animal fats, because oxygen is absent. Some crude oils, however, contain sulfur compounds. Coal-oil cannot be saponified by NaHO or KHO, and by this negative property we distinguish the mineral oil from vegetable or animal oil. (See further on.)

Refining of crude oil. The crude oil is stirred together with concentrated sulfuric acid. By this treatment the objectionable sulfur compounds are converted into a solid, resinous body which settles

with the acid, and the cleansed oil is drawn off. The latter is then subjected to the action of steam heat in large iron tank-boilers, and later on to direct fire. Thus are obtained the conventional fractions: 1. *Petroleum ether*, a colorless, very mobile oil of pleasant odor and intoxicating effect, passes over up to 70° C. This oil is much used as a solvent for fats and other bodies. 2. *Gasoline* distills between 70° C. and 90° C. 3. *Benzine* distills over between 90° C. and 150° C. After this is collected 4. *Kerosene* between 150° C. and 300° C. This portion is most valued for burning in lamps, because its *flash-point* is high and it is therefore *safe*. 5. *Lubricating oil* distills between 300° C. and 400° C. 6. *Vaseline* distills next and condenses as a semi-solid in the receiver. 7. Beyond this comes off considerable *paraffin*, a perfect solid (see under tar); a black, spongy residuum remains in the still.

Determining the flash-point of a given coal-oil. Pour the oil into a small tin-cup, which stands upon a water bath. With one hand hold a thermometer into the oil, with the other pass a lighted match across the surface of the oil. Note the temperature of the oil at which the vapor above the oil catches fire. This temperature is known as the flash-point and should not be below 60° C. for a safe burning oil.

NATURAL GAS.

Any bore-hole which is driven into sedimentary rock-formation can be expected to produce gas, provided the strata have not been disturbed much from

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their original horizontal condition. *Natural gas* has been found by many analyses to be composed chiefly of marsh-gas (CH_4). If it burns with a sooty flame then there are some of the higher members of the paraffine series present, each as C_2H_6, C_3H_8 . . . Sometimes there is free hydrogen present and in rare instances CO has been found with the marsh-gas.

CHAPTER XVIII.

THE HOMOLOGUES OF CELLULOSE—STARCH, DEXTRIN, SUGARS.

So cunning is the work of nature that extraordinary changes are constantly brought about in properties with apparently the same material. The study of a *wheat grain* will illustrate this. Fig. 99 repre-

FIG. 99.
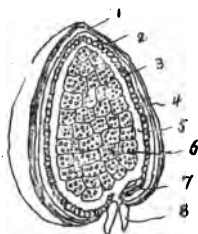
sents the section through the axis of the grain in magnified dimensions. Beginning from the outside there are 3 layers of small, attached cells *1, 2, 3. 1, 2* epicarpium or skin, colorless cells. *3* the endocarpium ; these cells contain a yellow coloring matter. *4* the embryo membrane, large cells, containing the nitrogenous body *gluten*, vegetable albumen. *5* a layer of amorphous substance, grey. *6* the meal-kernel made up of large, loose cells, and these cells

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are filled with a multitude of white globules which globules constitute what is known as *starch*. 7 is a dark-colored cell, known as the *embryo* or *germ*.

When such a wheat grain is soaked in water or kept wrapt in a wet cloth the grain swells and two sprouts appear at *8*, that is, the vital power lying dormant in the protoplasm of the germ cell awakes in presence of water. Cell upon cell is shot outwards until two blades of grass appear above the earth, which gradually develop into a full plant. The material for these cells was drawn from the store of starch and albumen, so cunningly provided within the reach of the embryonic cell within the grain—a veritable fodder-sack.

The starch, amylum. A white, very finely granular substance. Under the microscope we see spheroidal granules built up from concentric layers. Feels soft to the touch. When pure has neither taste nor smell. Is insoluble in cold water. *Hot water* swells the granules until they flow together into a shapeless, transparent paste, starch-paste. The paste dries into a yellowish, hard, horn-like body. The paste is slightly soluble in water, giving a clear solution upon standing. Starch develops in the roots of certain plants, namely, such plants which grow from the root just as well as from a seed—*potato, arrow root, sago.* The seed grain of Indian corn is richer in starch than other seed grains. Hence starch is made from either corn or potatoes. The corn is ground, while the potatoes are cut into a pulp by rotating knives, after a thorough

washing, to remove adhering soil particles. The pulp becomes milky; the milky liquid is strained off through a very fine hair sieve. The sieve retains the cellulose or skin portions, and also the gluten. The milky liquid is allowed to stand, when the white starch will settle to the bottom and is collected after drawing off the water. The starch only needs drying to be at once a commercial product.

Chemical properties of starch. (1) The analysis (same as for cellulose) leads to the ratio $C^6H^{10}O^5$, that is to say, identical with cellulose. Note nature's trick to give two very different bodies the same composition. Such bodies are named *isomeric* bodies. (2) A solution of iodine in alcohol or in water, solution of KI colors the starch, first purplish-red, and then blue. Heating causes the color to fade, but on cooling the color reappears. Very characteristic reaction for the identification of starch. (3) Starch dissolves in cold, concentrated HNO^3. The addition of water throws out a white precipitate, a nitro-body similar to gun-cotton, but non-explosive. Boiling very dilute acid (2–3 per cent.) changes the starch into dextrin and finally into glucose. The word starch (stark = strong in German, because starch paste stiffens tissues).

Dextrin (from *dexter* = right-handed). A gum-like, syrup-like substance, or dry granular. Much used in place of gum arabic (postage stamps, envelopes), because cheaper and more reliable. It forms from starch, either by heating the dry starch to 210° C. or by moistening the starch with 2 per cent.

HNO^3 solution, and then heating to 110° C. (best method), or by boiling starch with 2 per cent. H^2SO^4 solution until the resultant liquid does not turn blue with iodine solution. Dextrin is $C^6H^{10}O^5$, the same as starch and cellulose. Another isomeric form. It is not soluble in alcohol, but easily soluble in water, rotates plane of polarization to right.

The sugars. These are bodies formed in the sap of the cells of certain plants; in the seeds (grape, orange, etc.); in the stem (cane, sorghum, sweet corn); in the roots (beets, carrots). All soluble in water; some crystallize, others are syrups; all possess a more or less sweet taste.

Cane sugar, $C^{12}H^{22}O^{11}$, *or* $2C^6H^{10}O^5 + H^2O$. Obtained by neutralizing the somewhat acid sap of the cane, the beet, the sorghum, the maple, by means of chalk ($CaCO^3$), and by evaporating the clarified liquid rapidly—best in a closed boiling pan from which vapors and air are steadily withdrawn by an air-pump (vacuum pan). From the thick syrup fall small crystals; can be obtained in large, very perfect monoclinic crystals by recrystallization, which are drained from mother liquor in centrifugal filters, and are then known as crude sugar (90–95 per cent.). The refineries remove the 5 or 10 per cent. of impurities. Cane sugar is easily soluble in cold water, 2 parts of sugar in one of water, much more soluble in boiling water, slightly soluble in alcohol, not in ether. Melts at 160° C., and on cooling forms a vitreous, glassy body —candy. Heated at 200° C. it becomes black

   THE HOMOLOGUES OF CELLULOSE.   343

sugar or *caramel* (black, horny). By destructive
distillation it forms bodies similar to those from
starch or cellulose. Cane sugar forms genuine com-
binations with K^2O, Na^2O, CaO, BaO, SrO, all sol-
uble in water. The combination $C^{12}H^{22}O^{11}.BaO$
is now much used in the refining process. Concen-
trated H^2SO^4 acts energetically on sugar, SO^2;
$H.CHO^2$ (formic acid) escape, a coaly residue re-
mains. Boiling $HNO^3 + H^2O$ converts sugar into
oxalic acid ($H^2.C^2O^4$), water, CO^2 and NO. A sugar
solution rotates the plane of polarization to the right,
like dextrin. If a solution of cane sugar be kept
digesting on the water bath with HCl, or H^2SO^4 (a
few per cent.), its right rotation diminishes and
turns finally into left rotation ; the sugar is *inverted*.

Glucose, grape-sugar, $C^6H^{12}O^6$ or $C^6H^{10}O^5 +$
H^2O. Is largely contained in honey and in all
fruits and berries. Crystallizes in small scaly forms.
Less soluble in water than cane sugar (1 glucose—
$1\frac{1}{2}$ cold water). More soluble in alcohol than cane
sugar. The crystals contain one molecule of H^2O.
Melts at 70° C. Does not taste as strongly as cane
sugar. Concentrated H^2SO^4 does *not* change glu-
cose into a coal-like mass; the glucose combines
with the acid to form *gluco-sulfuric acid*. Glucose is
found in the urine of persons who suffer from *dia-
betes*. Copper sulfate + glucose + potassium hydrate
+ water gives at ordinary temperature red or yellow-
red cuprous oxyd. Cane sugar gives such a result
only by continued boiling. This reaction is the
best to distinguish the two sugars from one another.

Large quantities of glucose are manufactured from corn-starch (in U. S.) and from potato starch, (Europe).

$C^6H^{10}O^5$, starch + water + H^2SO^4 + boiling heat = $C^6H^{12}O^6$, glucose + H^2SO^4.
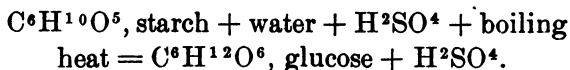
Mix 600 grs. of starch with 700 c.c. of luke-warm water into a milk. Mix 100 c.c. of water with 5 c.c. of conc. H^2SO^4. Heat the latter to boiling. Let the milk flow into the boiling liquid, but not so fast as to interrupt the boiling motion. Keep boiling for 3 hours, replenishing the water lost by evaporation. Perfect solution of glucose. Neutralize acid with chalk while boiling. Filter through bone charcoal ; evaporate to thick syrup and let cool. In the course of 10 to 12 hours the syrup will change to a stiff mass of small crystals of grape-sugar. Glucose is largely used as a substitute for malt in the brewing of beer, also as an addition to grape juice before fermentation into wine. By heating cellulose with dilute H^2SO^4 under pressure in closed boilers, it changes slowly into glucose (saw-dust made into sugar).

Fruit-sugar, syrup, levulose, $C^6H^{12}O^6$. Gives the slimy consistence to honey. Contained in all berries and fruits with the glucose. Does not crystallize. Rotates plane of polarization to the left. Invert sugar (see above) contains this variety of the family. It combines with 3 molecules of CaO to a water-insoluble body, while the isomeric cane sugar gives a soluble compound with CaO. The so-called *molasses*

or *melasse* in French, is largely composed of this sugar.

Milk-sugar, lactose, $C^{12}H^{22}O^{11} + H^2O$. Obtained in hard, colorless, tetragonal crystals, by evaporating the liquid obtained by straining curdled milk. Is only soluble in $6\frac{1}{2}$ parts of cold water. Agreeable sweet taste, but not as strong as the isomeric cane sugar. Does not melt, but loses the water of crystallization at 130° C.

Gum arabic, arabin, $C^{12}H^{20}O^{10} + H^2O$. Contained in the sap of many plants. It flows from the bark and is found adhering in gum drops to the bark of the stem or the twigs. Specially plentiful in the sap of the acacia trees. Forms with little water a thickish, sticky solution. Not soluble in alcohol. Does not reduce CuO to Cu²O as does dextrin. Furnishes about 3 per cent. of ashes.

CHAPTER XIX.

ALCOHOL, SPIRITS OF WINE, ETHYLHYDROXYD, C²H⁵(HO).

THIS important substance is a derivative of the sugars, and especially of glucose—grape-sugar. The grape-juice is essentially a dilute solution of glucose, has a pleasantly sweet taste. When this solution remains standing, uncovered, in a warm place (20° C. to 30° C.), it soon becomes turbid, and gas bubbles arise from the liquid more and more abundantly until the liquid begins to froth. As gradually as this action has increased it decreases, leaving a clear liquid, upon which rests a reddish or brownish scum, while a similar material has gone to the bottom. The liquid has now assumed a sour taste, but very agreeable, and when taken in large quantity produces stupefaction (drunkenness) ; the liquid is then known by the name of *wine* (Latin = *vinum*).

Arab experimenters were first in trying to get at the understanding of this remarkable action. They succeeded, by distillation, in separating the active principle of wine in form of a colorless liquid, very mobile, and of agreeable odor but burning taste. They found that this liquid will burn with a bright and very hot flame. The name *al-Kohol*, the *breath spirit* (from *spirare*, to breath) was given to this re-

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markable liquid. The Latin translator of the Arabic treatise translated al-Kohol into *spiritus vini*, French, *esprit de vin;* German, *weingeist* (the spirit or soul of the wine). However, in recent years the chemists of all nations use the word *alcohol* exclusively.

The process described above, by which a solution of sugar converts itself into a solution of alcohol, is now everywhere known as *fermentation*, the Germans alone use an indigenous word *gaehrung*. But similar processes are known to yield other products than alcohol ; hence, to be clearly understood, we say *alcoholic fermentation*. The chemical process of this fermentation is of the simplest.

$$C^6H^{12}O^6, \text{ glucose } + \text{ water} + \text{ferment} = 2C^2H^5(HO),$$
$$\text{alcohol } + 2CO^2.$$
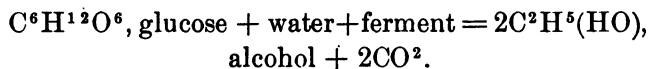
The gas bubbles forming in the process are CO^2. The *ferment* or *yeast* is found in the matter, which causes the turbidity of the fermenting liquid, and which either rises to form the scum or sinks to form the sediment. This matter is biological ; it is alive. Under sufficient magnifying power the scum differentiates itself into *cells*, single or in clusters. The cells have an envelope of cellulose, and are filled with a clear liquid. The liquid contains *protoplasm*, which can be separated as white flocculæ. The white substance dries into a horny body, the analysis of which gives $C = 55$; $H = 7.5$; $N = 14$; $O + S = 23.4$. In this body rests the life-potency of the cell. The cells multiply by " budding," as shown in Fig.

100.   A yeast cake is merely a multitude of such cells with some potato starch.   Botanists classify these yeast cells as the lowest form of the order *fungi.*   The specific name is *saccharomycetes cerevisiæ.* Because such cells are in the air with other minute
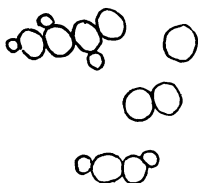
dust, the fruit juices begin to ferment, apparently by themselves, but if filter paper be tied over the vessel, no fermentation takes place.   The addition of yeast merely accelerates the process.

The manufacture of ethyl-alcohol.   It sometimes pays to distill wine (in France), but only in exceptional cases.   The bulk of the alcohol is made from grain or potatoes.   The process is essentially identical for all raw materials.   It comprises the following operations: (1) *Grinding* of the grain without sifting off the bran.   (2) *Mashing* of the grain with *malt.*   Under the word *malt* is understood sprouted barley dried after sprouting, and ground.   The sprouting of the barley grain develops another mysterious substance—*diastase*—which possesses the power to change starch into glucose more rapidly than sulfuric acid.   Its composition is not known, *not* supposed to be a living thing as yeast.   10 parts

of grain, 1 part of malt, 80 parts of water heated by steam in a tub to 75° C. until the conversion of the starch is completed ; that is mashing.

(3) To cool down the mash to 18° C. and transfer it to fermenting vats through a strainer. (4) Addition of sound yeast and fermentation of the *wort* (technical name of the strained mash) in a separate room in which the temperature is kept evenly at 20° to 25° C. The end of the fermentation is indicated by the collapse of the froth over the liquid.

(5) Distillation of the alcoholic liquor in copper stills. Alcohol boils at 78° C., water at 100° C. From the boiling mixture more alcohol passes into vapor than water. If the liquor contains 5 per cent. alcohol, then this entire quantity will have gone over when 28 per cent. of the liquid has distilled, leaving 72 per cent. of liquid in the still. (This residue is not thrown away, but used in mixing the feed for fattening cattle.) The distillate contains now 20 per cent. alcohol ; is milky from minute drops of amyl-alcohol (fusel-oil), and not saleable. It must be redistilled, yielding a 40 per cent. brandy, and this again distilled to get a 60 per cent. spirit, and this again and again until a *95 per cent. proof spirit* results. Beyond this the water cannot be eliminated by distillation alone.

By mixing with fused $CaCl^2$, or calcined copper vitriol, $CuSO^4$, the water is taken up by these bodies, and another distillation yields *absolute alcohol*, $C^2H^5(HO)$. The latter is only needed for special chemical purposes. The process of concentrating

the alcohol by distillation is called *rectification*.   To save the largest part of the fuel required, many improved processes have been invented, which at last resulted in an apparatus yielding proof spirit at the first operation.   This is done by carefully cooling the vapors in an apparatus of large cooling surface, *the dephlegmator*, known also as a *column apparatus*, which stands directly above the still.   Fusel oil and other complex side-products are removed from the alcohol in the dephlegmator.

Properties of alcohol.   A colorless, mobile liquid; remains liquid even at —90° C.; boils at 78.4° C. Specific gravity at +4° C. = 0.8095, at +15° C. = 0.795.   100 vols. at +4° C. give 109 vols. at 78°. Expands therefore thrice as much as water.   Taste, burning.   Pure alcohol destroys the organisms, is poisonous; dilute alcohol causes intoxication.   It is a solvent for many substances which are not soluble in water—its chief use in the laboratory.

Chemical constitution: Analysis gives simply the atomic ratio C^2H^6O.   But we write instead (C^2H^5) (HO) because alcohol acts towards acids like the hydroxyds of metals.   In this last form alcohol is meant to appear as the hydroxyd of the monovalent radical (C^2H^5).   But the latter may be looked upon as a complex radical made up of the simpler hydrocarbons $CH^3.CH^2$, or we may say that ethyl alcohol is equal to two groups of methyl in which one H is represented by the monovalent (HO)

$$\begin{cases} CH^3 \\ CH^2.HO. \end{cases}$$
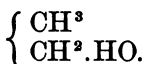
One hydroxyd can take up one hydrogen of an acid, hence when we act upon alcohol with conc. H^2SO^4, we obtain $2(CH^3.CH^2.HO) + H^2SO^4 = (CH^3.CH^2)^2.SO^4 + 2H^2O =$ ethyl sulfate or $CH^3.CH^2.HO + HCl = CH^3.CH^2.Cl + H^2O =$ ethyl chlorid. Such bodies were formerly named *ethers*, now they are named *esters*, *i. e.*, salts in which the metal is replaced by a compound carbon radical. When alcohol is heated in air or oxygen, its elements become oxydized, it *burns*, producing much heat.

$$CH^3.CH^2.HO + 6O = 2CO^2 + 3H^2O.$$
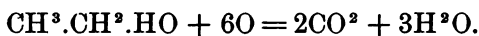
The absolute heat effect, $A = 2 \times 12 \times 8240 + 6 \times 34000 = 401760$ heat-units, or *one gram* of alcohol, by burning, will raise the temperature of 97.99 grams of water from 0° C. to 100° C., if no heat be lost by radiation and conduction.

CHAPTER XX.

SOME IMPORTANT DERIVATIVES OF ALCOHOL.

Ether, sulfuric ether, ethyl oxyd, $C^4H^{10}.O$. This very important substance originates thus :

$$2C^2H^5(HO) + H^2SO^4 = (C^2H^5)^2SO^4 + 2H^2O.$$
$$(C^2H^5)^2SO^4 + H^2O + heat = C^4H^{10}O + H^2SO^4.$$
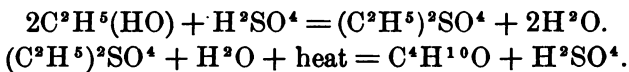
Bring into a boiling flask 100 grams concentrated H^2SO^4, 20 grams of water and 50 grams of absolute alcohol. This will give ethyl sulfate. Now close the neck with a three-hole stopper. Pass through one hole a long-stemmed funnel, through the second hole a thermometer down into the liquid ; through the third hole a knee-shaped gas evolution tube, and connect the latter by means of a proper reducer with a condenser. Heat until the thermometer shows 140° C., and maintain this temperature by letting in absolute alcohol. Ether + water will go over steadily and collect in receiver. Shake the distillate with $Ca(HO)^2$ + water, *milk of lime*, to neutralize acid particles. Separate the upper stratum of the two liquids with syphon. It contains some water. By redistillation in presence of CaO (burnt lime) the ether is obtained pure, CaO uniting with the water and binding it.

Ether is a thin, very mobile, colorless liquid, of

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strong, penetrating, but agreeable odor. Sp. G. =
0.736. Boils at 35° C., hence very volatile. Mixes
with alcohol in all proportions, but does not mix
with water. 10 parts of water dissolve 1 part of
ether. It dissolves many bodies which are neither
soluble in alcohol nor in water, notably fats. It
ignites easily and burns with luminous sooty flame;
be careful in avoiding open flames in the neighbor-
hood of evaporating ether.

It is evident that ether stands to alcohol in the
same relation as potassium or sodium oxyd to
potassium or sodium hydroxyd,

$$\left.\begin{matrix} K \\ K \end{matrix}\right\} O, \ \left.\begin{matrix} K \\ H \end{matrix}\right\} O, \ \left.\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}\right\} O, \ \left.\begin{matrix} C^2H^5 \\ H \end{matrix}\right\} O.$$
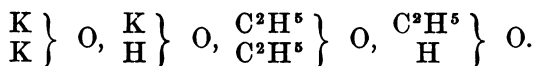
After once being separated it does not show any
tendency to reconvert into alcohol.

Ether produces unconsciousness, stupefaction,
when the vapors are taken into the lungs; it is an
anaesthetic.

Chloroform, CHCl³, can be considered as marsh
gas in which 3H have been replaced by 3Cl. It
results when 4 parts alcohol, 3 parts water and 1
part bleaching lime are heated in a flask or retort to
the boiling point. With the water is found in the
receiver a heavy, oil-like liquid—chloroform. The
reaction may go thus:

$$C^2H^6O + 2Ca(ClO)^2.CaCl^2 = CH^2Cl^2 + 3CaCl^2 + CaCO^3 + 2N^2O.$$

$$2CH^2Cl^2 + Ca(ClO)^2CaCl^2 = 2CHCl^3 + CaCl^2 + Ca(HO)^2.$$

23
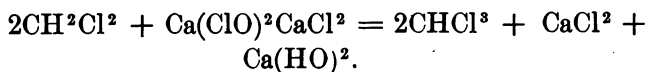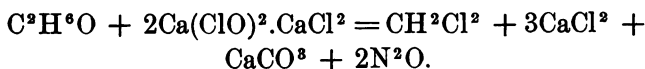
Colorless, thick liquid. Odor pleasant, taste sweet. Insoluble in water. Specific gravity $= 1.48$. Boils at $61°$ C. Its vapors are more poisonous than ether; it was formerly much used as an anaesthetic.

Iodoform, CHI^3. A yellow solid in scaly crystals. Insoluble in water, in acids, in alkalies. Soluble in alcohol and ether. Used much in medicine as an antiseptic for burns and wounds. It originates similarly to chloroform. From a mixture of alcohol, KOH or NaOH and iodine. First forms $K(IO) + KI$. Then KIO acts on the alcohol just as $Ca(ClO)^2$ does. Work out equation.

Aldehyde, C^2H^3HO. A thin, mobile, colorless liquid. Boils at $21°$ C. and has a suffocating odor. Specific gravity $= 0.801$. Origin: $C^2H^5HO + MnO^2 + H^2SO^4 + Aq = C^2H^3HO + MnSO^4 + 2H^2O + Aq$. In presence of air it changes into acetic acid, $C^2H^3HO + O = C^2H^3O^2.H$. It is therefore a strongly *deoxydizing* body. A glass plate can be made into a silvered mirror by pouring upon the well-cleansed surface a liquid composed of $AgNO^3 + NH^4HO + C^2H^3HO +$ water. In this liquid we have $Ag^2O.2NH^4HO + NH^4.NO^3 + C^2H^3HO +$ water. Now $Ag^2O.2NH^4HO + C^2H^3HO = Ag^2 + NH^4.C^2H^3O^2 + NH^4HO + H^2O$.

Chloral, C^2Cl^3HO. A colorless, thin liquid. Has a penetrating odor, attacks mucus membrane. Soluble in water. This solution does not give a white precipitate of AgCl when $AgNO^3$ solution is added. We explain this by saying that chlorine is *intraradical*, inside of the radical, not in the form of

chlorid. Specific gravity 1.502. Boils at 94° C. It is prepared by passing dry chlorine into absolute alcohol until the evolution of HCl stops: $C_2H_5HO + 8Cl = C_2Cl_5HO + 5HCl$. When chloral is taken in small doses (dissolved in water), it causes a peculiar intoxication and indifference to pain. For this purpose it is given by physicians, but it can become a dangerous habit for the patient.

Mercuric fulminate, Hg.C²N²O². Discovered by Howard, A. D. 1800. Liebig and Gay-Lussac found correct composition. *Properties.* Minute, white, needle-shaped crystals. Soft to the touch. Sweetish metallic taste. Little soluble in cold, more in boiling, water. Specific gravity = 4.42. *Very poisonous.* In the dry condition it explodes violently by friction, by a blow, or by concentrated H_2SO_4.

$$Hg.C_2N_2O_2 + blow = Hg + 2CO + 2N.$$
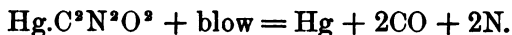
By experiment 1 gram furnished 78 c.c. of gas with a heat generation of 403.5 cal. or enough to heat the products of combustion of explosion to a temperature of 4200° C. Although gun-cotton gives more gas per unit, yet the explosive effect of the fulminate is much greater. This effect is often called by the French expression *brisance.* We say: Mercuric fulminate is the most *brisant* explosive. Why? Probably because of its instantaneous break-up into gas.

Preparation. We dissolve 5 grams of mercury in 60 grams of HNO_3 specific gravity 1.34 (45 c.c.) which gives us $Hg(NO_3) + HNO_3 + N_2O_3 + NO +$ water. When the metal is dissolved we cool the

liquid to 70° C. We bring 50 grams of 90 per cent. alcohol into a strong, well-tempered, ½-liter, round flask and pour the first liquid slowly into the alcohol while rotating the flask. A colorless mixture results. Should no reaction develop at once we place the flask upon a water-bath until small bubbles begin to show. Then we set the flask under strongly drawing hood or out of the window. Usually a very violent reaction sets in with large masses of white fumes emerging from the flask. When the reaction is over a white, flour-like precipitate of the fulminate is found on the bottom of the flask. We cool the liquid to ordinary temperature and more fulminate precipitates. Then we pour off the supernatant liquid, wash the crystals with cold water until the acid reaction ceases, collect the powder on a filter and dry it on the water-bath or better yet, in a current of warm air, or still better we keep it wet.

Manufacture of percussion caps. To reduce the brisance and to obtain a more penetrating flame jet, the fulminate is mixed with 30 per cent. of niter for mining caps, or 30 per cent. of potassium chlorate for dynamite igniters. 1. The materials are moistened with 30 per cent. water and mixed with wooden rubbers upon a polished slab of marble. 2. The paste is pressed through hair sieves and thus becomes granulated. The granules are very carefully dried, spread upon paper. The dry granules are sifted through hair sieves to remove the dust particles. 3. The granules are filled into the caps by special machines. The sheet copper is 0.26 mm.

thick.   The head has a small cavity Fig. A (Fig. 101).   Into this drop granules to the extent of 15 milligrams Fig. *B*; a stamp presses a thin copper foil over the charge Fig. *C*, and the cap is ready. This latter is the most dangerous of the operations.

FIG. 101.
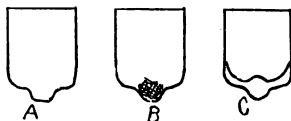
Since the charges are small, not much damage can ensue.   Heavy charges are fired with larger caps containing 300, 500, 750 mgs. of fulminate charge. Torpedo caps contain as much as 1,500 mgs. of fulminate.

Silver fulminate, $Ag^2.C^2N^2O^2$, has similar properties.

CHAPTER XXI.

SOME ORGANIC ACIDS.

We find these acid bodies chiefly in the flesh of berries or fruit, in the free state or in the form of salts—esters. There is a multitude of them and only the most important ones can be mentioned here.

Formic acid, ant acid, $H.CHO^2$. A colorless, mobile liquid of very pungent acid odor. Solid at $-1°$ C. Boils at $100°$ C. Specific gravity $= 1.235$. Causes a blister on the skin. Found in pyroligneous acid (wood distillation). Causes the stinging sensation produced both by ants and nettles. It forms in many ways by the oxydation of organic bodies, especially the carbohydrates. Most interesting is the synthetic formation by the action of CO gas upon KOH at $100°$ C. Thus:

$$KOH + CO = K.CHO^2 \text{ (potassium formate)}.$$

Then $K.CHO^2 + H^2SO^4 + heat = KHSO^4 +$
$$H.CHO^2.$$
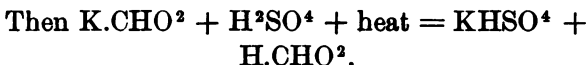
And also $CO^2 + 2K + H^2O = K.CHO^2 + KOH$. Formic acid precipitates many metals from the solution of their salts in metallic form. $HgO + H.CHO^2 + heat = Hg + H^2O + CO^2$.

Acetic acid, $H.C^2H^3O^2$ or $(CH^3)COOH$, a colorless, mobile liquid of pleasant, pungent odor. Solid

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at $+ 15°$ C. (glacial acetic acid), boils at $109°$ C. Sp. gr. at $18°$ C. $= 1.063$. On adding water the specific gravity increases until 1.0748 is reached (acid $= 78$ per cent., water $= 22$ per cent.), then the gravity decreases with the addition of water until 1.00 is reached. Hence it follows that one specific gravity may mean two very different acids; for instance, 1.069 can mean an acid of 96 per cent. and an acid of 33 per cent. An acid of 54 per cent. has the same specific gravity as acid of 100 per cent. Glacial acetic acid destroys the skin as readily as oil of vitriol. The vapor of the acetic acid burns. Acetic acid dissolves many oils which are insoluble in water. *The acetates of all metals are easily soluble in water*, hence, lead is usually employed in the form of acetate.

Acetic acid finds not only much use as vinegar, but also in the chemical laboratories and in the chemical arts, such as dyeing and printing. It is the oldest acid known to man, as it forms naturally when sugar solutions stand in a warm place in contact with air. This change does not take place unless a peculiar fungus — *mycoderma aceti* — is present.

$$C^2H^5.HO \text{ alcohol} + O^2 + \text{ferment} + \text{water} =$$
$$C^2H^3O^2.H \text{ acetic acid} + H^2O.$$
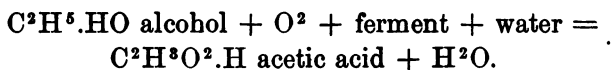
Pure acetic acid for laboratory use is prepared by distilling two molecules of crystallized sodium acetate with one molecule of concentrated sulfuric acid in glass retorts; in iron retorts for commercial use.

The latter are furnished with an alembic or helmet made of tin.

$$Na.C^2H^3O^2 + H^2SO^4 + heat = H.C^2H^3O^2 + NaHSO^4.$$
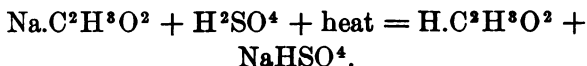
The sodium acetate is, at this time, obtained exclusively from pyroligneous acid. (See distillation of wood or cellulose.) The pyroligneous acid is first made into $Ca(C^2H^3O^2)^2$, evaporated to dryness, and the mass gently roasted to destroy tar oils. Thereupon distillation with HCl yields fairly pure acetic acid, containing water. This acid is neutralized with Na^2CO^3 and the $Na.C^2H^3O^2$ is allowed to crystallize. The crystals are distilled with H^2SO^4.

Manufacture of vinegar. Raw materials are all kinds of alcoholic liquids, especially wine, cider, spoilt beer, and fermented worts from the glucose industry. a. *From wine.* In open barrels, into which wine and vinegar are filled. The vinegar brings with it the ferment. The latter grows rapidly into a thick skin over the whole surface. Vinegar is finished in 8–14 days according to temperature of the room, or the outside air. b. *From dilute alcohol, by the rapid process.* The barrel B, Fig. 102, is open at the top. At F, F' are perforated wooden discs, so-called *false bottoms*, the space between the two discs being filled with clean pine shavings. The latter are soaked with good vinegar, and upon the top layer is sown a culture of pure mycoderma cells (all other germs are excluded). The alcoholic liquid is then distributed by the holes in F' over

the surface of the shavings, while plenty of warm air enters through the holes *1, 2, 3, 4*, etc. The acidified liquid is drawn from the spigot into the pail, and returned to the top of the barrel as many times as may be needed to convert the whole of the alcohol.

FIG. 102.
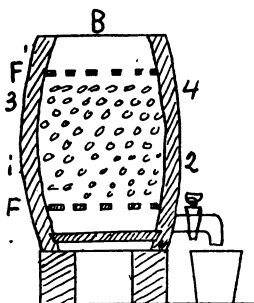
It is possible to make the resulting vinegar as strong as 30 per cent., in which form it is known as spirit vinegar, which for cooking purposes is diluted with 10 parts of water.

Oxalic acid, $H_2.C_2O_4$. At ordinary temperature a white, or colorless solid. Forms readily large crystals, monoclinic with 2 molecules of water of crystallization. $H_2.C_2O_4 + 2H_2O$. The crystals show a sharp, sour taste, *no odor*. Soluble in 10 parts of cold water, in three parts of boiling water. Soluble in $2\frac{1}{2}$ parts of cold alcohol, in 1.8 parts of boiling alcohol. The crystals lose their water of crystallization at 60° C. At 97° C. the crystals melt, at higher heat break up into $CO_2 + CO$ and $H.CHO_2$ (formic acid). In a current of air the anhydrous

acid can be sublimed at 150° to 155° C. The vapors attack the mucous membrane and are poisonous.

Chemical properties. Oxalic acid is not a good solvent for the metallic oxyds and metals, because the oxalates are either quite *insoluble* or but little soluble in water. The most insoluble oxalate is calcium oxalate $Ca.C^2O^4 + 2H^2O$, (quadratic crystals). This salt is not soluble in acetic acid but soluble in HCl. Oxalic acid is therefore our best agent for separating calcium from a solution. Oxalic acid decomposes quickly in presence of an oxydizing agent.

$$H^2.C^2O^4 + O = H^2O + 2CO^2.$$
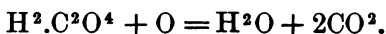
It precipitates gold and platinum from their chlorids.

$$2AuCl^3 + 3H^2C^2O^4 + water = 2Au + 6HCl + 6CO^2$$
$$PtCl^4 + 2H^2C^2O^4 + water = Pt + 4HCl + 4CO^2$$
$$H^2C^2O^4 + H^2SO^4 + heat = CO^2 + CO + H^2SO^4.H^2O$$
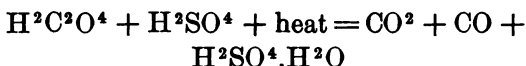
(best way to get pure CO for experiments, the CO^2 being removed by means of NaHO).

Occurrence of oxalic acid. It is found in the saps of many plants, as $KH.C^2O^4$, especially in the leaves of sour clover (oxalis), and in rumex ; also in rhubarb (as CaC^2O^4). It forms the calculi in the bladder and kidneys of man.

Manufacture. There are two ways. (1) By action of nitric acid upon the carbohydrates—sugar, starch, wood,

$C^{12}H^{22}O^{11}$, sugar $+ 12HNO^3 +$ water $=$
$6H^2C^2O^4$, oxalic acid $+ 11H^2O + 12NO$.
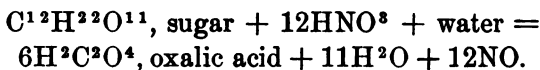
Theoretically 1 part of sugar requires 2.21 parts of
HNO^3 or 5 parts of 50 per cent. acid. Practice
shows that 6 parts are needed to effect complete oxy-
dation. Reaction is energetic after once started.
When evolution of gas has gone down, put flask on
flame and boil until volume of liquid is $\frac{1}{3}$ of original.
On cooling, the acid crystallizes. (2) By action of
KOH + NaOH upon sawdust or similar refuse
wood. The action is probably as follows:

$C^6H^{10}O^5$, cellulose $+ 2KOH + 2NaOH +$ heat $=$
$Na^2.C^2O^4 + K^2CO^3 + 2CH^4 + CO + H^2O. + 4H$.

The temperature should not be above 240° C. to
obtain the best result. At a higher temperature
$Na^2C^2O^4$ changes to $Na^2CO^3 + CO$. When all the
wood is changed, let cool. Extract with little cold
water, which dissolves only K^2CO^3. Then dissolve
residue in boiling water and stir with an equivalent
of $Ca(HO)^2$.

$Na^2C^2O^4 +$ water $+ Ca(HO)^2 +$ boil $= Ca.C^2O^4 +$
$2NaHO$.
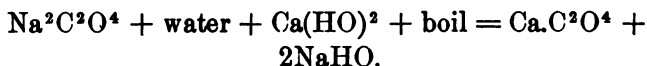
Filter. Filtrate is evaporated for next batch.
Residue is decomposed by dilute H^2SO^4 giving
$CaSO^4 + H^2C^2O^4$. Separate the liquid (hot) from
the solid $CaSO^4.2H^2O$ by means of a filter press or
centrifugal. Evaporate filtrate until crystals appear,
then let cool, and the bulk of the oxalic acid will fall
out, and after air-drying can be packed and shipped.
In spite of the many operations, this second method

gives the acid at considerably less cost than the first method.

Lactic acid, milk acid, $H^2.(C^3H^4O^3)$. A colorless, thick liquid. Strong sour taste; no odor when pure. Specific gravity $= 1.25$. Soluble in water, alcohol, ether. When the water-solution is evaporated a part of the acid escapes with the vapor, but most of it remains as a syrup. At 130° C. it loses one H^2O and becomes so-called anhydrous acid, $C^6H^{10}O^5$ (isomeric with glucose, starch).

Lactic acid can be separated from other acids by the insolubility of some of its salts, especially $Sn.C^3H^4O^3$. The calcium lactate is somewhat soluble in cold and more soluble in hot water. Lactic acid is found in sour milk; in the gastric juice; in certain fermented vegetables, such as cabbage and turnips. It forms easily from glucose or any other sugar in presence of the *lactic ferment.* The latter is obtained from rotten cheese or rotten meat.

Tartaric acid, wine acid, $H^2.C^4H^4O^6$. As solid, in colorless, monoclinic crystals. Easily soluble in water, much less in alcohol, and not at all in ether. The water-solution rotates the plane of polarization to the right. Strong sour taste. Melts at 170° C., forming a vitreous body—meta-tartaric acid—without decomposition. If we add tartaric acid to a solution containing a ferric or aluminic salt, and then an excess of NH^4HO, there will be no precipitate, enabling the chemist to effect certain separations, otherwise difficult.

Salt of seignette, $Na.K.C^4H^4O^6 + 8H^2O$. Large crystals showing orthorhombic hemihedry.

Calcium tartrate, $Ca.C^4H^4O^6 + 8H^2O$ forms by adding lime water to a tartrate solution. Insoluble in water.

Tartar emetic, $K(SbO)C^4H^4O^6 + \frac{1}{2}H^2O$ soluble in 14 parts of cold water, in less boiling water. Obtained by boiling a solution of ordinary tartar ($K.H.C^4H^4O^6$) with Sb^2O^3, the teroxyd of antimony. Used as an emetic; causes death in larger portions.

We obtain the tartaric acid from the tartar or argol which is the name of the hard, stony deposit in the casks in which the grape juice has been fermenting. The Germans call it *weinstein*, winestone. The crude tartar is a mixture of the acid potassium tartrate $KH.C^4H^4O^6$ with coloring material and yeast cells, and calcium tartrate. The tartrates were originally dissolved in the juice but had to fall out in measure as the percentage of alcohol increased, they being insoluble in the latter.

We boil the fine powder with 15 parts of water for some time, add bone-black or charcoal which absorbs the coloring matter, and filter boiling hot. From the filtrate precipitate small crystals of $KH.C^4H^4O^6$. They go under the name *cream of tartar*. We redissolve in boiling water, add one equivalent of $Ca(HO)^2$ and keep boiling until we have KOH + insoluble $Ca.C^4H^4O^6$. We separate by H^2SO^4 after filtering, getting $CaSO^4.2H^2O$ + $H^2.C^4H^4O^6$, and proceed the same as for oxalic acid.

The crude tartar is used in assaying as a deoxydizing agent and alkaline flux, for on heating in a

covered crucible to redness a decomposition takes place,

$$2KH.C^4H^4O^6 + \text{red heat} = K^2CO^3 + 3C + 4CO + 5H^2O.$$
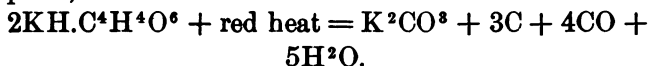
Both C and CO act as deoxydizers upon metallic oxyds; while K^2CO^3 can take up sulfur or silica, or both.

Citric acid, $H^3.C^6H^5O^7$. A tribasic acid. Large colorless crystals, orthorhombic combinations $H^3.C^6H^5O^7 + 2H^2O$. Very sour taste. Easily soluble in water and in alcohol. The acid acts in iron solutions and aluminum solutions the same as tartaric acid. It is used for a number of medical preparations, especially seidlitz powders, magnesium citrate and others. Contained in sour lemons, in gooseberries.

Preparation. The juice is pressed from sour lemons, strained and neutralized with $Ca(HO)^2$. The calcium citrate is nearly insoluble in water, and is decomposed like the tartrate and oxalate with H^2SO^4.

Malic acid, $H^2C^4H^4O^5$. Imperfect crystals, resembling cauliflower. Deliquesces in the air, forming a syrup. Very sour. Soluble in alcohol. Occurs in many fruits, especially in sour apples, plums, gooseberries, etc. Calcium malate is easily soluble, and forms large crystals. This enables the separation of the acid. Insoluble lead malate is, as a rule, prepared and decomposed with H^2S.

Tannic acid, tannin, $C^{14}H^{20}O^{18}$. An amorphous powder; color pale-yellow or brownish; somewhat

shining. Taste very astringent. Very soluble in water, barely soluble in ether, very slightly in absolute alcohol. Its water-solution gives with $FeCl^3$ or with $FeSO^4$ a blue-black color and later a blue-black precipitate, insoluble in water. Its solution gives a flocculent precipitate with a solution of gelatine. If a piece of fresh skin or hide is placed in the tannin solution, the tannin will gradually leave the liquid and precipitate itself on the skin. The tannin is easily oxydizable, and therefore reduces CuO to Cu^2O in presence of NaHO, or KHO, and gives Ag with $AgNO^3$, same as glucose. Hence chemists place the tannin among the *glucosids*. Its chief use in medicine is as an *astringent* in affections of the mucous membrane. It is used to make our ordinary *black ink*. We obtain the tannin from the so-called Turkish nut-galls. The latter form on the leaves and twigs of certain plants, especially oak and acacia, after a sting has punctured the leaf. The sting comes from wasps mostly, who deposit their eggs in the outflowing sap. The sap hardens and forms the nut-like excrescence or growth. The nut-galls contain as much as 65 per cent. of tannin.

Preparation. We extract the ground galls with a mixture of 30 volumes of crude ether (0.74), 4 volumes of water, 1 volume of alcohol (90 per cent.). The extract separates into a lower layer, a syrup (tannin and water) forming the upper layer is composed of ether-alcohol with a little tannin and all other bodies. The water-syrup is evaporated and leaves shining amorphous tannin.

Recipe for black ink.   125 grams of ground nut galls, 24 grams of copperas ($FeSO_4 + 7Aq.$) 24 grams gum-arabic, 1 liter of water, 1 gram of creosote.   Boil the materials for 1 hour, replacing the evaporating water.   Strain through a hair sieve or through muslin.   Let settle for a week, then put up into bottles.

Tanning bodies similar, yet not quite identical with tannin are contained in the barks of many trees, especially the oak, the hemlock, the willow.   In the tanneries the hides are first cleansed from the hair and adhering parts of flesh, together with the uppermost layer of cells—the cuticle—by scraping.   The clean skins are spread in water-tight pits so that a layer of ground bark is between two skins, as many as 100 skins in 1 pit.   Then the pit is filled with water and allowed to stand quietly for several months, the longer the better.   The water draws the tanning bodies from the bark and the skins take it from the water-solution.   By cutting off a bit of the skin one recognizes from the cross section, whether the change has taken place to the very core.   Then the skin has become *leather*.   It is perfectly proof against putrefaction.   It has become impenetrable to water and yet it remains pliable when dried.   A similar change takes place in the skin in presence of alum, ferric sulfate, and chromium sulfate.   So that we have now tan, iron, chrome, alumina leather.   The scarcity of bark has brought into use these substitutes.

Gallic   acid, $H.C^7H^5O^5 + H^2O$ crystallizes   in

silky needles of the triclinic system. Colorless or pale yellow. Soluble in 3 parts of boiling water, slightly soluble in ether or alcohol. Action on metallic solutions in presence of $NaHO$ or KHO or NH^4HO like tannin, somewhat more energetic. Forms well crystallized metallic salts. It is found ready in sumac and other plants. Prepared by allowing a solution of tannin to cover itself with fungi (mildew) in presence of yeast.

Pyrogallic acid, pyrogallol, $H.C^6H^5O^3$. A fluffy mass of thin scales and needles. Soluble in 2.2 parts of water at 15° C. Solution colorless. $FeCl^3$ gives a blue color with this body; free N^2O^3 produces a brown color. All oxydizing agents produce a brown color. An alkaline solution turns brown at once in air. It acts more energetically upon metallic solutions than the preceding ones. This gives its high value as a *developer* in photography. Here the $AgBr$ on the plate becomes changed by the action of light and becomes capable of decomposing water in presence of pyrogallate. $2(AgBr)$ active $+ H^2O + Na.C^6H^5O^3 = Ag^2 + 2HBr + Na.C^6H^5O^4$ (the brown body); the ordinary $AgBr$ is not changed.

Preparation. By heating gallic acid thus:

$$H.C^7H^5O^5 + H^2O + \text{heat} = H.C^6H^5O^3 + CO^2 + H^2O,$$
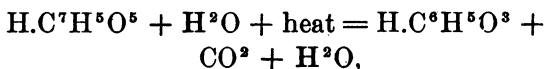
hence name *pyrogallic* from *pyro* = fire.

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CHAPTER XXII.

THE VEGETABLE FATS AND ANIMAL FATS.

MANY plants develop in their seeds an oily sub-stance, in the place of starch, for the nutrition of the embryo plant; the cotton, flax, hemp, rape, sesame, anise, poppy, mustard, and among the trees all the so-called nut-bearing kinds: palm, walnut, beach, hickory, olive, plum, peach, almond and many others, while some grow oil-bearing roots such as the pea-nut. After removing the hard shell from the nuts the soft kernels are crushed between rolls of iron or stone, the pulp is warmed to about 60° C, put into strong hair cloth and pressed by mechani-cal or hydraulic devices. The oil runs off. The remaining cake is very nutritious, containing still a good deal of oil. It is often fed to the cattle, or used as manure after the oil has been fully extracted with carbon disulfid. Immense quantities of these oils are made annually in Europe; in the United States cotton-seed oil and linseed oil (flax) are the only ones. Most of the plant oils remain thick liquids at ordinary temperature, some become pasty (palm-oil) and a few are solids.

All fats and oils repel water, and are practically insoluble in water. They dissolve in alcohol, in ether and in carbon disulfid. Their specific gravity

is mostly smaller than that of water. Between the fingers they produce a slippery sensation, hence they lubricate, *i. e.*, reduce friction. They taste pleasantly or unpleasantly, and each oil has a different odor or flavor. However, taste and flavor are produced mostly by small quantities of special oils, —flavoring oils—*essential oils*, while the mass of the fat varies but slightly in composition and quality, yet often considerably in the relative quantities of its constituents. Hence each oil has a specific boiling-point, and also a different fluidity—*viscosity*—which is measured by the quantity of the oil which will run through a nozzle of standard diameter in one minute at standard temperature.

The animal organism develops fat upon and between the muscles, in the hollow bones, partly as lubricant, partly as a non-conductor of heat, partly as a food store (sick persons lose their fat first, because the body lives upon it when the digestive organs are out of gear). The nerve substance, brain substance is fat, and the yoke of the egg is a yellow liquid fat upon which the embryo of the oviparous animals feeds. Viviparous animals have no eggs, because the embryo cell receives its nourishment from the mother's blood through the navel chord.

The animal fats are solid at ordinary temperature or at any rate pasty. The fat lies in form of globules within a loose tissue of large cells. In heating the fat the cells break, the globules unite into one mass and the cell substance (fibrin, chondrin), coagulates and comes to the surface as brown scum.

Otherwise the animal fats act like the vegetable fats or oils.

Chemical action of fats. . The fats prove themselves to be *esters* or salts, in which fat acids of the marsh gas series, $C^nH^{2n}O^2$, with high value of n, are united with *glycerin*, which has the properties of a triatomic alcohol.

$$\text{A fat is } G{\overset{\displaystyle A}{\underset{\displaystyle A}{<}}}A \text{ or } G.(\bar{A})^3$$
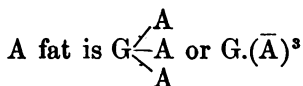
when G stands for glycerine and $\bar{A}$ for a monatomic fat acid radical. This view is deduced from the action of metallic hydroxyds upon the fats. (1) NaOH + Aq + fat + boiling heat yields after sufficient boiling a thick paste, *soap*, which is *completely soluble* in much water, and quite soluble in a few volumes of alcohol. Upon adding HCl or H^2SO^4 (dilute) to the solution in water, a white flocculent body separates. If the liquid be heated to near boiling point, the white substance melts, rises to the surface and forms there a layer of oil. On cooling the oil becomes solid or semi-solid, and represents the fatty acids. The liquid contains NaCl + HCl + water + glycerin. The *glycerin* was discovered by the Swedish chemist Scheele about 130 years ago. Being an apothecary he had to make adhesive plasters by boiling olive oil or other fats with lead oxyd. In this process the fat acid combines with PbO into a pasty, sticky body, which is quite insoluble in water. Spreading the paste upon linen, muslin or silk, makes the plaster.

Now Scheele noticed one day that the water, with which he had washed the plaster, possessed a sweetish taste, and this led him to work until he had separated this sweet body in the form of a thick liquid, by evaporation ; and because of the sweet taste he named it glycerin from *glucos* = sweet. He knew it was not sugar because it would not give alcohol with yeast. The composition and chemical nature was established long afterwards by J. Liebig and others. Accordingly, we know at present that glycerin has a composition represented by the symbol $C^3H^8O^3$; that towards acids it acts like a base—a hydroxyd, with 3 replaceable hydrogen atoms, and hence we write: $C^3H^5(HO)^3$ with the probable constitution $CH^2(HO).CH(HO).CH^2(HO)$.

Properties. At ordinary temperature a syrup. At a very low temperature an orthorhombic solid, which only melts at 17°–20° C. Boils at 290° C., and distills without decomposition ; more readily in a current of steam. At 150° C. it ignites on approaching a flame and burns with a pale blue, non-luminous flame. If salts are present the glycerin breaks up during the distillation, thus $C^3H^8O^3$ + heat = $C^3H^4O + 2H^2O$. The product is *acrolein*, a very disagreeably smelling substance (the odor arising from a glowing wick). Glycerine mixes with water in all proportions, is soluble in alcohol. Not soluble in ether nor in chloroform. Pure glycerine is hygroscopic, attracts water from the air, hence it causes a burning sensation on the mucous membrane. Diluted with 1 volume of water it is pleasant on a chapped

skin because it does not become dry, keeps the new skin from chafing. Chemical reaction : A borax bead moistened with glycerin colors flame green; without glycerin colors flame orange-yellow.

Preparation. Boil 90 grams of olive oil with 50 grams of lead oxyd and 50 grams of water until the oil has disappeared, the plaster formed. Then add more water, boil a few minutes, let cool and drain the water through a filter. Pass H_2S through the liquid to remove any dissolved lead, filter, evaporate below the boiling-point, and at last heat the syrup at 100° C. to constant weight.

Manufacture of glycerin is a part of the manufacture of stearic, oleic, and palmitic acids. These reactions constitute the base of the process :

1. Saponification as above with hydroxyds.

2. Stearate + H_2SO_4 + water + heat = stearic acid + glycerin + sulfate + water.

3. Stearin + water + heat + pressure = stearic acid + glycerin + water.

The last reaction gives the best results. It is carried on in 2 cylindrical steel-plate boilers. As much as 1000 lbs. of fat can be taken at one operation. The boilers stand one above the other vertically, and communicate by means of 2 tubes so that the materials circulate and the temperature equalizes. The temperature is 200° C. and the pressure accordingly 15.3 atmospheres or about 230 lbs. per sq. inch. Time of action 10 hours. The molten fatty acids collect above the watery glycerin, the latter is drawn off at the bottom, evaporated in a vacuum,

and furnishes at once a commercial glycerin.   It has a yellow color and contains quite a number of other organic bodies in small quantities.   Best purification by means of crystallization at $+ 2°C$. and separation of crystals from mother-liquor by means of centrifugal machine.

Tri-nitro-glycerin, $C^3H^5(NO^3)^3$, an oily liquid at ordinary temperature, but capable of solidification below the freezing-point.   Insoluble in water. Easily soluble in ether.   Very explosive by friction or blow.   Begins to vaporize at 75° C.   The vapors when taken into the lungs cause headache, sick stomach.   Tri-nitro-glycerin influences the action of the heart, and is used by physicians in cases of collapse.   It has become the most important explosive for blasting since Nobel conceived the idea of letting the oily nitro-glycerin be soaked up by *infusorial earth* (4 parts of the oil, 1 part of the earth).   In this form it is known as *dynamite*.   The white blasting powder now in use in many mines contains: Nitro-glycerin 45–55 per cent.; soda niter 25–30 per cent.; wood pulp 15–20 per cent.; magnesia 2–3 per cent.   Wood pulp takes the place of infusorial earth, and the niter burns up the wood in the explosion.   Such a composition is not as effective as dynamite, but on the other hand it can be handled with less danger, and it does not shatter the rock as much as dynamite.   Nitro-glycerin dissolves gun-cotton, yielding a jelly-like material known as *blasting gelatine*.   The latter can be changed into a hard, horny material, granulated,

and then forms, with the addition of ammonium picrate, the so-called *smokeless powder*.

Manufacture of nitro-glycerine. Reaction:

$$C^3H^5(HO)^3 + 3HNO^3 = C^3H^5(NO^3)^3 + 3H^2O,$$

temperature 10° C. to 20° C. Operation: Prepare a mixture of 30 parts of 95 per cent. H^2SO^4 with 28 parts of fuming HNO^3 (Sp. Gr. 1.48). Cool this mixture to 10° C., weigh out 10 parts of glycerin, stir together with 0.3 parts of concentrated H^2SO^4. Pour the glycerin sulfate in a thin stream, or drop by drop, into the acid mixture while stirring the latter with a thermometer. The temperature rises— should it rise above 20° C., stop pouring and cool the liquid, then finish pouring. The result is an emulsion or milky liquid which soon begins to separate into two distinct layers. The upper layer is tri-nitro-glycerin; the lower layer is sulfuric acid, which retains some nitric acid. After some hours' standing the acid part is discharged from the mixing vessel, and the nitro-glycerin run into cold water, washed several times, and finally with a 5 per cent. solution Na^2CO^3 to remove last traces of acid. There must be no brown fumes during the mixing. Their appearance means danger. The sulfuric acid serves to take up the $3H^2O$ of the process, so that the HNO^3 retains its concentration. It can be used over and over if the water is boiled out of it.

Tallow (from beef or mutton) contains three different fats: 1. *Stearin,* $C^3H^5.(C^{18}H^{35}O^2)^3$, *glycerin tri-stearate.* A hard, white crystalline solid at ordinary temperatures; melts at 55° C. then returns

to solid condition, but at 71.6° C. is permanently liquid.

2. *Palmitin, $C^3H^5.(C^{16}H^{31}O^2)^3$, glycerin palmatate.* Scaly crystals; white, luster of mother of pearl. Melts at 46° C., then solidifies, and becomes permanently liquid at 62.8° C.

3. *Olein = $C^3H^5.3(C^{18}H^{33}O^2)$, glycerin tri-oleate.* Pure olein, is a colorless oil without either taste or smell. In contact with air it absorbs oxygen and turns " rancid " by separation of " free " oleic acid. Oleic acid belongs to the series $C^nH^{2n-2}O^2$.

Soap, saponification. Soap results from the change of the glycerin esters into sodium or potassium esters, by the action of NaOH or KOH :

$$C^3H^5.(C^{18}H^{35}O^2)^3, \text{ stearin} + 3\text{NaOH} =$$
$$3\text{Na}(C^{18}H^{35}O^2), \text{ soap} + C^3H^5(\text{HO})^3 \text{ glycerin.}$$
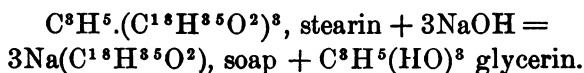
890 parts of stearin require 120 NaOH ; 100 parts of stearin require 13.4 parts NaHO and furnish 10.3 parts of glycerin ; while the quantity of soap depends upon how far the water is removed by the process of boiling and salting, for in a solution of NaCl soap is more and more insoluble as the percentage of NaCl rises in the liquid. This distinguishes soft from hard soap. The process of changing fat into soap is named *saponification.*

Drying oils. The oils from flax seed, poppy seed and some other plants, differ from other oils in so much as they become dry in a day or two when spread over wood or any other solid material. The surface has become covered with an elastic film. A second

and third coating increases the thickness of the film. The latter shows luster and is known as *varnish*. Other oils, such as olive oil, nut oil, etc., do not dry, they turn rancid and continue to be greasy for a long time. Hence linseed oil or poppy seed oil is used as the liquid medium in painting. The oil is mixed intimately with the colored solids oxyds, salts, earths after the latter have been ground to exceedingly fine grain. The chemical reason for this drying lies in the fact that the chief part of drying oils is made up of *linolein* instead of olein. *Linolein* is C^3H^5.-$(C^{16}H^{27}O^2)^3$. The linoleic acid is $H(C^{16}H^{27}O^2)$ and is known as an unsaturated acid belonging to the series $C^nH^{2n-4}O^2$. The acid absorbs oxygen rapidly and becomes *oxylinoleic acid;* the latter being the varnish.

Turpentine, spirits of turpentine, resin, balsam. All coniferous plants exude from their bark an oily liquid, which soon becomes sticky and ultimately a transparent solid. The pitch-pine of the Southern States and the Canadian balsam fir produce this material more abundantly. By means of cuts in the trees the liquid is collected in the woods (same as maple sap). It is usually a thick liquid of pale yellow color and strong pleasant odor. This turpentine or balsam contains an oil named spirits of turpentine and a solid known as *resin* or *rosin*. The oil is obtained by distillation, usually in a current of steam. The residue contains several similar bodies insoluble in water, but soluble in part in absolute alcohol, and partly insoluble. The Canada

balsam contains oil = 24 per cent.; resin soluble in absolute alcohol = 60 per cent.; insoluble resin = 16 per cent.   Spirits of turpentine, a clear, colorless, mobile liquid, sharp taste, peculiar pleasant odor.   High refraction.   Insoluble in water, little soluble in alcohol, easily soluble in ether, chloroform, carbon disulfid.   Boiling-point varies between 160° to 180° C.   Specific gravity=0.85 to 0.89.   Rotates plane of polarization.   The substance may be represented as a hydrocarbon, $C^{10}H^{16}$, but is evidently a mixture of several hydrocarbons, which have not been separated from each other.   Turpentine evaporates very rapidly in air at ordinary temperature and leaves a *film*.   Hence it is known by painters as a *quick dryer* when used for diluting paint.   Its chief use is in the manufacture of different varnishes, because it dissolves the resins.

Rosin, pine rosin, colophony.   Obtained from the heating or distilling of the turpentine.   A hard, brittle substance, of yellow to brown color, sticks to the mortar and pestle when grinding.   Specific gravity 1.01 to 1.08.   Insoluble in water.   Softens when heated, then melts.   Soluble in spirits of turpentine, in absolute alcohol, in ether, etc.   Chemically this substance must be considered as an acid —alcoholic solution reddens litmus.   This body has been named *abietinic acid*, $C^{44}H^{62}O^{4} + H^{2}O$. It combines with the metallic hydroxyds to form soluble and insoluble salts, esters.   With KOH or NaOH results soluble (water) potassium or sodium abietinate; with $Ca(HO)^{2}, Pb(OH)^{2}$, etc.,

result insoluble bodies. The acid is, therefore, analogous with the fatty acids. Rosin is frequently added in soap-making.

Pitch is the name given to the somewhat elastic body obtained by the destructive distillation of rosin, or resinous wood.

There are a great many other rosin-like substances from other plants, each with peculiar properties. They are all used in making varnishes.

Rubber, caoutchouc, gutta-percha. Obtained by evaporation of the milky sap of certain tropical trees, and of immense importance to modern civilization. The gutta-percha tree is from 40–70 feet high. The leaves are inverted, oval and leathery. By means of incisions at different heights the sap is made to flow. It sets or coagulates shortly after leaving the tree and then dries out into a tough, elastic, light-colored, leathery substance which is impermeable to water, therefore even the natives knew how to make flasks and bottles of it. Rubbing causes negative electrification. Very poor conductor. In contact with air it absorbs oxygen, increases in weight, becomes brittle. Under gentle heat the gutta-percha becomes soft and plastic, whence its great serviceability. Melts at 120° C. into a thin liquid ; at higher heat forms vapors of a disgreeable odor. The analysis of pure gutta gave C, 86.36 ; H, 12.15 ; O, 1.49. The great mass of the gutta is probably a hydrocarbon, the oxygen belonging to a secondary body. C^6H^{10} is probably the nearest approach to the formula. The gutta is somewhat

soluble in absolute alcohol. Easily soluble in chloroform and carbon disulfid.

Under the name *caoutchouc* (Indian) goes a variety of rubber which comes from the milk-sap of a number of trees belonging to different families and quite unlike the gutta plant. Some of the trees are of enormous size, 135 feet high, 25 feet diameter. One tree can produce as much as 60 lbs. of rubber per year without suffering. The fresh sap has an acid reaction. Contains in 100 parts caoutchouc $= 31.5$; albumen $= 2.0$; a bitter substance $= 7.0$; insoluble in water and alcohol $= 3.0$; water $= 56.5$. Handling of sap : The sap is mostly spread upon boards and dried upon a slow fire ; the resulting film is drawn off, and many films are kneaded into one mass with water. By another method the sap is allowed to stand 24 hours. The rubber rises to the top and looks like cream, (a double volume of water having been first added). The water is let out at the bottom and fresh water is added until it runs off clear. A solution of alum is then added to the cream, and the the caoutchouc separates. It is kneaded to remove the liquids and then dried, but often retains much water when it reaches the factory.

Caoutchouc contains the hydrocarbon C^6H^{10} in varying proportion depending on the species of plant, upon the local climate, the soil, and especially the treatment of the sap. Physical properties : High elasticity, transparency in thin sheets. Indifference towards acids and alkalies except the concentrated H^2SO^4, HNO^3 at elevated temperature. Easy adherence of two fresh surfaces (making of

tubes). Impermeable to water, but permeable to gases. Pure rubber changes on exposure to light and air into a more or less brittle body. Can be restored somewhat by exposure to the vapors of alcohol.

Vulcanizing of rubber. The fact that rubber becomes soft and smeary at a relatively low heat reduces its usefulness. This defect can be remedied somewhat by impregnating it with sulfur. In molten sulfur the the rubber takes up as much as 15 per cent. S. But it also absorbs sulfur if the latter in the form of fine powder is kneaded together with the fine-cut rubber and then rolled out into sheets or blocks. Thus prepared the material is less permeable to gases and does not get smeary when warmed. Ink eraser is made by adding fine quartz sand to the sulfur. Zinc oxyd, or prepared chalk are kneaded into the rubber to make strong tubes and steam-packing washers. A solution of sulfur in CS^2 or SCl^2 in contact with fine-cut rubber gives sulfur to the latter. The actual vulcanization consists in *heating* (baking) the impregnated rubber to a temperature of from 146° to 170° C.

Hard rubber, ebonite. A horn-like, usually black substance in which one does not recognize any of the usual properties of rubber. Replaces wood, glass, leather, horn, ivory for many articles, notably combs. Can be pressed to assume almost any shape. Excellent non-conductor for electricity. 6 parts of rubber are kneeded with 3 parts of sulfur, 1 part of zinc sulfid or other material, then heated for several several hours to 140° C., and pressed in iron moulds.

CHAPTER XXIII.

ORGANIC ALKALOIDS.

THESE bodies are of special interest as strong stimulants or direct and fatal poisons. Combine with acids to form easily crystallizing salts nearly all soluble in water. Some turn red litmus to blue. They are the direct products of certain plants, in which they are found as salts of organic acids.

Theobromin, $C^7 H^8 N^4 O^2$. The stimulating substance in cocoa and hence in chocolate. Is very slightly soluble in water, its reaction is neutral.

Caffein, $C^8 H^{10} N^4 O^2$. The stimulant in coffee and in tea. The tea-leaves contain as much as 4 per cent.; the coffee bean only one per cent. It is not a strong base ; the salts are decomposed by water.

Urea, $CH^4 N^2 O$. Colorless, orthorhombic prisms. Specific gravity 1.45. Taste cooling like niter. Easily soluble in water. Reaction neutral. Combines with acids to salts, which are mostly little soluble in water, especially the precipitates produced by $AgNO^3$ and $Hg(NO^3)^2$. Urea is the principal substance contained in urine.

Morphin, $C^{17} H^{19} NO^3$. White or colorless ; little soluble in water, but easily soluble in acids. Is a narcotic or sleep producer ; overdose is fatal. Contained in opium, and opium itself is the result from

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drying the sap which runs from unripe seed cap-
sules of the poppy.

Chinin or Quinin, $C^{20}H^{24}N^2O^2$. White solid,
slightly soluble in water with blueing of litmus;
strong base. Easily soluble in acids—chinin sul-
fate forms white, fluffy needles, and is usually taken
as a remedy for malaria or other fevers. Chinin is
extracted from the bark of a shrub growing in Peru.

Strychnin, $C^{27}H^{22}N^2O^2$. Colorless prisms, nearly
insoluble in water and only slightly in alcohol or
ether. Soluble in acids. The sulfate is used in
medicine in minute doses. 50 milligrams of the
sulfate constitute a *fatal dose*, inasmuch as the
strychnin causes terrible convulsions and lock jaw.
It is developed in the fruit and seeds of the strychin
plant.

Brucin, $C^{23}H^{26}N^2O^4 + 8H^2O$. Colorless tetra-
gonal prisms. Easily soluble in alcohol and ether,
slightly soluble in water. Reaction: Brucin +
HNO^3 gives *red body*, which turns into a purple
precipitate on adding $SnCl^2$. Made use of to detect
nitrates. Brucin is found with strychnin in the
beans of the *Strychnos Ignatii*. Brucin is poisonous
but not so violently as strychnin.

Atropin, $C^{17}H^{23}NO^3$. Needle-shaped prisms,
silky luster. Tastes very sharp and bitter. Salts
do not crystallize readily. Is very poisonous. When
applied in dilute solution to the cornea of the eye the
pupil becomes enlarged, so that the iris seems to dis-
appear. It is extracted from the cherry-like fruit of
atropa belladonna, (belladonna signifies handsome

lady—because the ladies of fashion have made use of the extract to make their eyes more fascinating).

Cocain, $C^{17}H^{81}NO^4$. Colorless prisms soluble in alcohol. Is extracted from the coca leaves. Produces local stupefaction of the nerves and is therefore used to relieve pain.

Nicotin, $C^{10}H^{14}N^2$. A colorless oily liquid, usually yellow because not quite pure. Odor penetrating, disagreeable ; soluble in water, in alcohol. Changes red litmus to blue. A strong base. Boils at 250° C. Very poisonous. A small dose acts as a narcotic. Extracted from the leaves of tobacco. Fine Havana tobacco contains only about 2 per cent. Coarse common tobacco as much as 7 per cent. A poultice of tobacco leaves on any part of the body can cause convulsions and even death. The smoking tobacco has been fermented, most of the nicotin is therefore destroyed and NH^3 is formed.

25

The animal body is composed, from the chemical standpoint, of fat, muscles, bone and derivatives of the muscles. The muscles or flesh, as well as the skin, hair, tendons, are composed of albumenoids; the bone is calcium phosphate.

Albumen, $C^{72}H^{112}N^{18}S^2O^{22}$. Is obtained by evaporating the white of eggs at a temperature not exceeding 50° C., and thus,

$$C^{72}H^{112}N^{18}S^2O^{22}$$

obtained represents a yellowish transparent mass with a specific gravity of 1.314. With water it swells and then dissolves. It has an alkaline reac tion (due to the presence of KOH and K salts). If the water solution be heated it begins to become turbid at 60° C. At 75° C. large flakes separate; the albumen is *coagulated,* and a faint odor of H^2S noticed. The addition of HCl, H^2SO^4, HNO^3 causes the coagulation without heating; the addition of KOH or NaOH prevents coagulation, even at boiling heat.

Basic lead acetate, $(HO)Pb.\overline{A}^2$, forms a precipitate with albumen. The percentage composition of dry albumen is: C = 53.4, H = 7.0, N = 15.6, O = 22.4, S = 1.6. The blood of all animals contains a

colorless substance which acts like the white of
eggs, and a similar body is contained in the sap of
all plants: they are known as *blood albumen* and
vegetable albumen.   What biologists call protoplasm
is chemically not distinguished from albumen, but
protoplasm has life and albumen has not.   To
find the conditions under which ordinary albumen
will change into protoplasm will be equivalent to
finding the source of life itself.   A very grand prob-
lem, and one which I think possible of solution,
though not probable.

All derivatives and homologues of albumen we
call *albumenoids.*

Haemoglobin, $C = 53.8$, $H = 7.3$, $N = 16.1$, $S =$
0.5, $Fe = 0.4$, $O = 21.9$.   This body gives the red
color to blood. Under the microscope a drop of
blood reveals a colorless fluid in which spheroid
red bodies float freely, together with pale bodies of
the same shape.   The first are known as the red
blood corpuscles, the second as the white corpuscles
or *leucophytes.*   Diameter about 0.013 mm.   The
bulk of the red corpuscles is water and haemoglobin.
Note the iron in the composition.   The red color is
due to this iron.   Haemoglobin absorbs oxygen,
nitric oxyd, carbon monoxyd, hydrogen cyanid.
The reason for the very fatal action of CO and HCN
upon man is probably due to this property of the
haemoglobin.   .

Haematin, $C^{48} H^{51} Fe^3 N^6 O^9$.   This is a genuine
chemical unit.   Blue-black of color, insoluble in
water, alcohol, ether.   Soluble in solutions of KOH

NaOH, NH^4HO. Also in dil. H^2SO^4. The alkaline solution is olive green in thin column and red in thick column. Obtained from haemoglobin.

Fibrin, C = 52.6, H = 7.0, N = 17.4, O = 21.8, S = 1.2. Fibrin is held in solution in the fresh blood. When blood is in contact with air for a short time it *clots*, becomes thick. Beating with a paddle separates from the blood a red, stringy, fine fibrous mass, which is fibrin mixed with haemoglobin. The clear liquid is named the *serum* of the blood, and contains the blood albumen and many other bodies besides the mineral salts. The muscles are chiefly modified fibrin, so called *hyssin, creatinin, sarkin, xanthine,* all albumenoids.

Casein (cheese stuff), C = 53.6, H = 7.1, N = 15.7, O = 22.6, S = 1.0. This body is found in the skimmed milk together with milk-sugar and salts. Casein is the chief nutriment in milk. It is well known that milk *curdles* and then has a sour reaction. The curds are composed of casein and water; the water can be removed by pressing and drying. Casein turns into cheese by the action of ferments.

Horn, hair, skin are all closely allied to albumen, although their chemical action is quite different, for these bodies are quite insoluble in water and in all agents except concentrated alkalies, which dissolve them and evolve NH^3 as other albuminoids.

	hair	horn	finger-nail	wool
C	= 49.8	50.7	50.2	49.8
H	= 6.4	6.7	6.8	7.0
N	= 17.1	17.3	16.9	17.7
O + S	= 26.7	25.3	26.1	25.5

Boiling water changes the skin into *gelatine* or *glue*. *Silk* is partly soluble in boiling water, which extracts *sericin*, $C^{15}H^{25}N^5O^8$, and leaves *fibroin*, $C^{15}H^{23}N^5O^6$.

Distillation of albumenoid substances. Animal charcoal. When albumenoid bodies, more particularly the hoofs and horns, and leather scraps of cattle are subjected to dry distillation, the succession of phenomena and the products are in general similar to those which we observed in the distillation of wood and coal, especially the latter. Yet the quality and quantity of the products are different.

The distillation furnishes (1) a black residue—animal charcoal; (2) a watery ammoniacal liquid, and oils (not tar); (3) gases of exceedingly strong and disagreeable odor. Animal charcoal contains more or less of the original nitrogen according to the degree of the temperature. Much of the nitrogen goes over as $NH^3.CO^2$ (carbamid) and $(NH^4)^2CO^3$. (This used to be the chief source of ammonium salts, hence the expression salts of and spirits of hartshorn).

All charcoal has the faculty of attracting coloring matter which may be either actually dissolved or only suspended in liquids; but animal charcoal, and

especially bone charcoal (bone-black), are more effi-
cent than wood charcoal.   The oil resulting from
this work is known as the *oil of Dippel*, or also
neat's foot oil much in use formerly as a lubricant
for clocks and watches and other delicate mechan-
ism.   It does not turn rancid, nor change into resin-
ous sticky substances as other oils do.

CHAPTER XXV.

ORIGIN OF CYANIDS.

WHEN potash (pearlash) is liquefied in an iron crucible or pot at a bright red heat and animal charcoal (except bone-black) be added, the charcoal disappears amid turbulent evolution of gas. (In practice the proportions of potash and charcoal vary, perhaps 1 : 1 is a good average.) If then the fused mass be digested with water, or boiled with the latter in the kettle or iron pot, and then allowed to stand quietly, there will be found, after several days, a crop of yellow quadratic crystals and a mother liquor containing K^2CO^3, K^2S, and some other bodies. This liquor, after evaporating to dryness, can be used in the next operation with fresh potash. The crystals are of exceeding interest. In the drug trade they are known as *yellow prussiate* of potash. The German chemist Diesbach, of Berlin, was the first who discovered that this salt gives with certain salts of iron a beautiful blue precipitate—known as *prussian blue*—but kept his knowledge as a secret; the Englishman Woodward, in 1724, published the first account of its preparation. In 1752, the French-man Nacquer obtained the pure salt, *the phlogisti-cated alkali*, but only through the genius and labors of Scheele (1732), of Gay-Lussac and Porret (1814),

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of Gmelin (1822), and lastly of Liebig, came to light
the true nature of this remarkable substance, which
chemists now call unanimously potassium *ferrocya-*
nate and give to it the symbol $K^4(Fe(CN)^6)$. The
symbol assumes the existence of a radical $(Fe(CN)^6)$
of the valence four. Within this larger radical
there are six units of the smaller radical $(CN) =$
cyanogen. The larger radical is ferro-cyanogen,
which some chemists write FeCy and therefore the
yellow crystals are $K^4FeCy + 3H^2O$. One sees
here the very positive iron become a part of a very
negative complex radical, in such a way that from
a solution of this salt the alkaline hydroxyds do *not*
precipitate any iron hydroxyd, nor does H^2S precip-
itate any FeS when passed into the alkaline solu-
tion. But for an understanding of this strange
complex it will be necessary to break down the com-
plex form in order to get at the fundamental unit
cyanogen.

Properties of potassium ferrocyanate.   Commonly
the crystals show a light lemon-yellow color ; color
is sometimes orange. The crystals are very cleav-
able parallel to the basal plane and the cleavage
plates are pliable, elastic. The salt dissolves in 4
parts of water at ordinary temperature, in 2 parts at
boiling temperature. It loses its water of crystal-
lization between 100° and 110° C. and becomes an
opaque, chalk-like mass. At red heat it melts and
decomposes with evolution of nitrogen gas, thus :

$$K^4(Fe(CN)^6) + \text{red heat} = 4K(CN) + 2C + Fe + 2N.$$
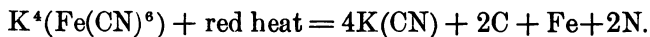
The fused mass is grey. Water extracts a colorless solution of $K(CN)$, *potassium cyanid*, leaving behind a black mixture of iron and carbon and iron carbid.

Potassium cyanid, $K(CN)$. $C = 18.4$, $N = 21.5$, $K = 60.1$. It is a white crystalline body. Easily soluble in water. Insoluble in 95 per cent. alcohol; but in warm 50 per cent. alcohol it is fairly soluble. On cooling the solution will deposit isometric cubes or cubo-octohedrons similar to KCl or NaCl. The salt itself as well as the solutions emit the strong and peculiar odor of bitter almonds, because the CO^2 of air decomposes the solution (and the solid salt in moist air also) thus:

$$2K(CN) + H^2O + CO^2 = K^2CO^3 + 2H(CN).$$
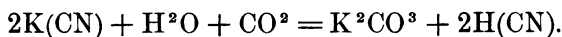
The odor is due to $H(CN) =$ hydrogen cyanid. The solution of $K(CN)$ in water does not bear heating, and therefore cannot be concentrated by boiling as other salt solutions, because the salt breaks up thus:

$$K(CN) + 2H^2O + water + heat = K(CHO^2) + NH^3 + water.$$
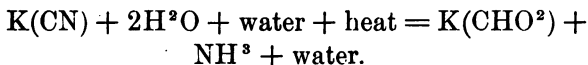
That is, potassium cyanid breaks up into potassium formate and ammonia. This behavior should be well remembered.

Preparation. Pulverize the yellow ferrocyanate coarsely. Heat in a flat, iron dish or pan to expel water of crystallization. The salt turns white. Fill it into an iron crucible, which stands in a furnace, after admixing dry pearlash in the ratio of 3 parts of pearlash to 8 parts of the dehydrated ferrocyanate. Cover with an iron lid and heat grad-

ually to yellow heat. The K_2CO_3 is added in order to save all the cyanid, thus:

$$2K_4(Fe(CN)_6) + 2K_2CO_3 + \text{yellow heat} =$$
$$10K(CN) + 2K(CNO) + 2CO_2 + 2Fe.$$
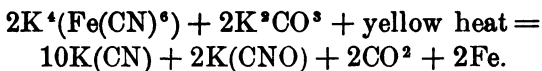
$K(CNO)$ is potassium *cyanate*. The product is thus a mixture of 5 molecules potassium cyanid with 1 molecule potassium cyanate. The cyanate is not harmful for any of the ordinary uses of the cyanid. In order to obtain pure KCN, the pearlash is left out. When the mass in the crucible fuses quietly, introduce a warm glass rod, and this rod, upon cooling, must be covered with a pure white film of the salts. Tap the crucible several times on the floor to cause a perfect settling of the iron particles and pour out into ingot moulds.

Chemically pure KCN can only be obtained by passing $H(CN)$ into a solution of KOH in alcohol, the liquid being kept cool. Then $K(CN)$ separates in small crystals. Collecting these upon a filter they can be melted into solid cakes of desired shape and size. $K(CN)$ is *very poisonous*. It is used to extract gold from the ores, because Au dissolves, forming a double cyanid, but only in presence of air thus:

$$2Au + 4K(CN) + H_2O + O = 2Au(CN).K(CN) +$$
$$2KOH.$$
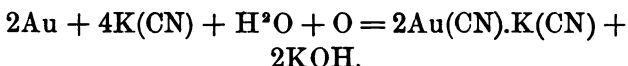
A very dilute solution such as 0.2 per cent. KCN is just as efficient as a strong solution. Silver dissolves similarly and all silver salts except Ag_2S and even the latter slowly in presence of air. Hence the

use of KCN in cleaning silverware, in fixing photo-graphic negatives. K(CN) is used as a solvent in electroplating with silver, with gold, and other metals. It is used for separating nickel from cobalt.

Hydrogen cyanid, prussic acid, H(CN), is at ordinary temperature a colorless liquid. Strong odor of bitter almonds or peach kernels. Boiling-point at 26.5° C., hence exceedingly volatile. One drop upon a glass slide solidifies from the sinking of the temperature due to the rapid evaporation. Point of solidification lies at − 15° C. Specific gravity = 0.696. H(CN) barely reddens blue litmus. This substance is so very dangerous that it should only be handled by very expert persons. Mixes with water and with alcohol in all proportions. The water solution exposed to light decomposes into a brown solid and NH^3, hence such solution should not be kept, but should be prepared whenever needed. The vapor of H(CN) burns with a *purple* flame. H(CN) is changed by concentrated HCl or H^2SO^4 into formic acid $H(CHO^2)$ and ammonium salt thus :

$$HCN + 2H^2O + HCl = H(CHO^2) + NH^4Cl.$$
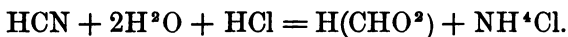
(Some water must be present).

That (CN) is a monad and combines with *one* H can be shown by decomposing one volume of the vapor or gas over mercury by K, when ½ vol. of hydrogen results. The water solution of H(CN) dissolves oxyds and hydroxids, forming metallic cyanids :

$$HgO + 2H(CN) = Hg(CN)^2 + H^2O,$$
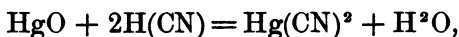
Mercuric cyanid which is soluble in water.

Preparation of H(CN). The reaction $HCl + K(CN)$ is not available, because the solution of $K(CN)$ does not stand heating. (See above.) But the yellow prussiate is available for this purpose, with the following scheme:

$$2K^4(Fe(CN)^6) + 3H^2SO^4 = 6H(CN) + 3K^2SO^4 + K^2(Fe^2(CN)^6) \text{ a blue substance.}$$
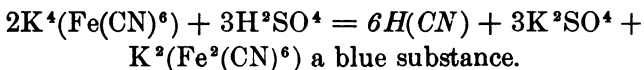
Recipe. Bring into a short-neck flask 30 grams pulverized yellow prussiate and a cooled mixture of 21 grams conc. H^2SO^4 with 42 c.c. of water. Connect with Liebig's condenser and let the end of the condenser tube dip just under the distilled water (25 c.c.) in the receiver. Then distill.

Cyanogen, C^2N^2. (Kuaneos = Cy.). This radical is at ordinary temperature a colorless gas of peculiar odor and very poisonous. The gas shows a sp. gr. of 1.806. It is inflammable and burns with *purple* flame. Under a pressure of 3 atmospheres it becomes a mobile liquid which turns into a mass of crystals at $-35°$ C. It is soluble in water and in alcohol.

Preparation. We heat in a small retort, or in a glass tube, mercuric cyanid (see above), the latter breaking up:

$$Hg(CN)^2 + heat = Hg + C^2N^2.$$
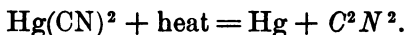
Composition. We collect the gas over mercury; add somewhat more than 2 volumes of O and $\frac{1}{2}$ volume (H^2+O) fulminating gas, and explode. We

introduce KOH to absorb CO^2. Next we introduce hydrogen, 2 volumes, and explode after reading the volume. From the contraction we find the remnant of O after first explosion ($\frac{1}{3}$ contraction and $\frac{2}{3}$ contraction for H consumed), and subtracting this from the remnant of N + H we get at the vol. of N, and in the absorbed vol. of CO^2 there is $\frac{1}{2}$ vol. of C. And then we find that 1 vol. cyanogen gives 1 vol. C + 1 vol. N, hence cyanogen in the free state is (C^2N^2) not (CN). It follows also that here is an exception to the law which we found previously. Here one volume of an element uniting with one volume of another element yields *two* volumes of the combination. In cyanogen the *two* volumes give only *one volume* of the product. This is verified by the volume weight of the gas, for.

1 volume of C weighs	1.072 grs.
1 volume of N weighs	1.250 grs.
1 volume of C^2N^2 weighs	2.322 grs.,

while the experiment gives 2.326 for one volume of cyanogen. Cyanogen combines with chlorine to form $(CN)Cl$, a terribly poisonous gas. It also combines with bromine.

Sulfocyanogen, $(CNS)^2$, forms colorless crystals.

Hydrogen sulfocyanate, $H(CNS)$, a colorless liquid of pungent odor like HCl and strong acid reaction.

Potassium sulfocyanate, $K(CNS)$. Colorless crystals; easily soluble in water and in alcohol. The solution of this salt gives with ferric salts a *blood-*

red solution in presence of free acid. Very delicate reaction.

Preparation. Fuse together $KCN + S$ in a crucible, dissolve in water and crystallize.

Potassium ferricyanate, red prussiate of potash, $K^6(Fe^2(CN)^{12})$. A beautiful salt. The crystals are of deep garnet-red color and dissolve very easily, with an intense yellow color, in water. The crystals contain no water of crystallization.

It is prepared by acting upon the solution of potassium ferrocyanate with chlorine; thus:

$$2K^4(Fe(CN)^6) + water + 2Cl = K^6(Fe^2(CN)^{12}) + 2KCl + water.$$
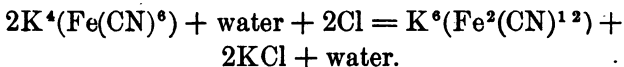
We say that 2 molecules of tetravalent ferrocyanogen have become polymerized—have coalesced—in one hexavalént radical, *ferricyanogen,* $(Fe^2(CN)^{12})$.

In qualitative analysis potass. ferricyanate serves to reveal the presence of a *ferrous* salt inasmuch as they combine to an intensely blue compound, thus:

$$K^6(Fe^2(CN)^{12}) + 3FeSO^4 + free\ acid + water = Fe^3(Fe^2(CN)^{12}) + 3K^2SO^4 + free\ acid.$$
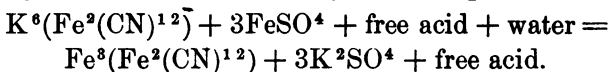
$Fe^3(Fe^2(CN)^{12})$ is known as a blue coloring material under the name of *Turnbull's blue.*

Potassium ferrocyanate gives with *ferric* salts a similar combination of equal intense blue color which is named *prussian blue.* The following equation represents this relation:

$$3K^4(Fe(CN)^6) + 4FeCl^3 + free\ acid + water = Fe^4(Fe(CN)^6)^3,\ prussian\ blue + 12KCl + free\ acid + water.$$
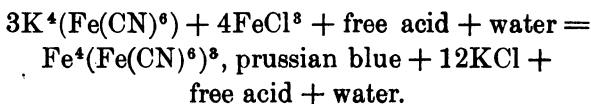
Of prussian blue as well as of Turnbull's blue there is a water-soluble variety, which results whenever an excess of the potassium ferro- or potassium ferricyanate is added to a ferric or ferrous salt. This soluble form is known as *wash blue* in the laundry business.

Potassium cyanate, K(CNO). This salt results when K(CN) is kept liquid in presence of air.

$K(CN) + O = K(CNO)$ at red heat.
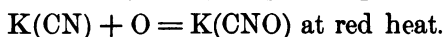
This strong affinity for oxygen is the reason why K(CN) is a most excellent agent for deoxydation at high heat. It is much used in assaying and in blowpipe work thus:

$SnO^2 + 2K(CN) + $ red heat $ = Sn + 2K(CNO)$.

$CuO + K(CN) + $ red heat $ = Cu + K(CNO)$.
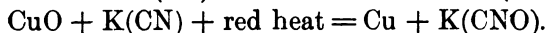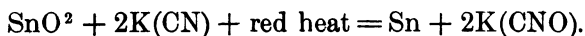
The aqueous solution of potassium cyanate breaks up even at ordinary temperature; when heated to boiling $NH^3 + CO^2$ escape and K^2CO^3 remains in the liquid.

$2K(CNO) + 3H^2O + $ heat $ = K^2CO^3 + CO^2 + 2NH^3$.
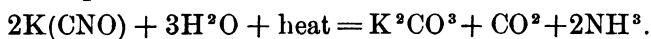
Hydrogen cyanate can be made, but is exceedingly unstable. It has an odor somewhat like a mixture of $SO^2 + HC^2H^3O^2$. It is very curious that if a solution of $(NH^4)(CNO)$, ammonium cyanate is evaporated, only water escapes, but the residue has all the properties of *urea, (CH^4N^2O)*, the principle secretion in the animal and human urine.

Cyanuric acid, $H^3(C^3N^3O^3)$ can be made in large colorless crystals. One recognizes that this is the formula of cyanic acid multiplied by 3. It results

from the heating of dry urea above the boiling-point, when NH^3 escapes and cyanuric acid is left.

Fulminic acid is not known in the free state. But we saw above that the analysis of the mercuric fulminate gives $HgC^2N^2O^2$. Now this radical ($C^2N^2O^2$) is just the double of the radical in (CNO) cyanic acid. Hence we have here an intensely interesting polymerism or equal percentage-composition for three totally different substances.

CHAPTER XXVI.

BONE-ASH AND PHOSPHORUS.

THE animal skeleton is composed of bones. The
bone again can be separated into a mineral part
(not combustible), into gelatine (glue) and into fat.
The fat may be extracted by any of its solvents
(carbon disulfid, ether, chloroform, etc.) The gela-
tine can be boiled out by water. If the bone after
extraction is merely dried and bleached it becomes
fit for conversion into useful and ornamental ob-
jects (by the lathe and by the carving tool). If it
be thrown into a hot furnace it will be converted
into *bone-ash*. With the latter and its chemical
nature, we shall now occupy ourselves.

Bone-ash is infusible and somewhat luminous
at a high temperature. It dissolves in HCl, in
HNO^3 + aq., but not in H^2SO^4. There is usually
a disengagement of CO^2 unless the burning of the
bones had been done at very high heat. In the
latter instance a small quantity of the ash will pro-
duce a brown spot (alkaline reaction) when placed
upon a strip of yellow turmeric paper. It acts thus
like CaO. The solution in HCl gives a white, gel-
atinous precipitate when $NH^4(HO)$ is added; there-
fore there must be an *acid* present of as yet unknown
properties, because the solution of calcite in HCl

or of $CaSO^4$ in HCl does not precipitate with
$(NH^4)HO$. The presence of calcium is, however,
made certain by the form of the minute crystals
which are separated upon adding conc. H^2SO^4 to
the HCl solution of the bone-ash. These crystals
are identical in shape with the calcium sulfate or
vitriol.

But since we have learned that oxalic acid forms
with calcium an oxalate which is not soluble in
water and not soluble in dilute acetic acid, we can
apply that knowledge right here to advantage. For
we find the precipitate which is thrown down by
NH^4HO in an HCl solution of the bone-ash to be
quite soluble in acetic acid. Adding a solution of
ammonium oxalate to the latter a bulky white pre-
cipitate falls and thus calcium in large quantities is
proved beyond any doubt. Let us designate the
unknown acid as A^x; then we can write a prelimi-
nary scheme for what we have thus far accomplished.

Bone-ash $= CaA^x$; solution of bone-ash in
$(m + 2)HCl = CaCl^2 + H^2A^x + mHCl$; the pre-
cipitate by NH^4HO must be CaA^x.

The acetic solution will be again

$$H^2A^x + mNH^4Cl + nNH^4(C^2H^3O^2) +$$
$$qH.C^2H^3O^2 + Ca(C^2H^3O^2)^2 + H^2O = \text{solution.}$$
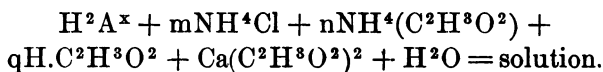
To this solution we add ammonium oxalate
$(NH^4)^2C^2O^4$, and thus we get a precipitate and a
liquid. The precipitate will be $Ca(C^2O^4)$, the liquid
will contain $H^2A^x + NH^4Cl + NH^4(C^2H^3O^2) +$
$H.C^2H^3O^2 + (NH^4)^2C^2O^4$ water. We filter and

evaporate to dryness.   Then we heat carefully over
an open flame, causing the volatilization of NH^4Cl
and of $NH^4(C^2H^3O^2)$; further increase of heat will
eliminate the excess of $(NH^4)^2\overline{O}$ and we will have,
probably, H^2A^x, the unknown acid, or perhaps
$(NH^4)^2A^x$; provided that this unknown acid does not
easily volatilize.   We find that a remnant is left;
that this remnant imparts a *green* color to the flame,
and that it dissolves in water, giving a colorless
solution which shows a strong acid reaction.   We
also find that the remnant does volatilize at a *red
heat*.   Thus we have established that this body is
probably an acid-forming, non-metallic, oxyd.   It
is not probable that any of the non-metallic elements
of our acquaintance could produce such a residue,
since their oxyds are very easily volatilized, or since
they form hydrogen compounds which are quite
volatile.   In order to separate the element a treat-
ment with strong deoxydizing bodies is indicated, to
wit, potassium, sodium, hydrogen, carbon, marsh gas.
Of these possible agents *carbon* is the only available.
(Reasons below.)   We make H^2A^x into a thick
syrup by using H^2SO^4 to precipitate the calcium
instead of using NH^4HO and $(NH^4)^2\overline{O}$, and then
evaporating.   Mix charcoal powder with it until a
sticky mass results.   Heat over open flame until
quite dry, and then fill the black mass into a tube, F,
Fig. 103, of hard infusible glass, which has been
closed at one end.   By placing the tube upon a
brick (1) against a second brick (2) and using a
Bunsen blowpipe on the closed end, we can bring

the tube to the required temperature. As the heat rises we begin to observe a peculiar odor at the mouth of the tube, and on approaching a taper a greenish flame develops, a white smoke rising into the air. At the same time wax-like drops condense in the forward part of the tube at (3). At length the flame burns more and more with a pure

FIG. 103.
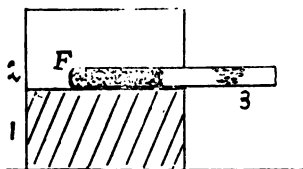
blue color (CO) and the action is complete. When the tube has become cold we cut off the forward part with a file stroke and a red-hot rod (glass or iron). The new substance is transparent or translucent. Its color varies from pale yellow to bright red. (Probably 2 different substances?) It is soft as wax. It emits a peculiar odor similar to that of *ozone*. A white fume arises from it steadily. It melts at 45° C., and begins at once to burn with a bright flame and evolution of white fumes. Under water it can be melted without danger of ignition. It dissolves somewhat in alcohol, more in fat oils. If such solution is rubbed over the hands or the face those parts will shine in a dark room with a pale green light. This property has been the justification for giving to this remarkable elementary body

the name *phosphorus* (*phos* = light; *phorus* = carrier). It would be more consistent to change the name to *phosgen,* and thus obtain a consonant series: Oxygen, hydrogen, nitrogen, chlorogen, bromogen, iodogen, fluogen, phosgen, and so forth.

(1). *Note.* Brand was the first to obtain phosphorus, in 1674, by distilling, in a clay retort, the residual mass from evaporated urine; but that bones contain much more phosphorus than does urine, was only discovered 100 years later by Scheele.

(2) *Note.* Experience has shown that a higher percentage of phosphorus can be obtained from bone-ash if only two-thirds of the calcium are removed by means of H_2SO_4, leaving soluble calcium phosphate to be separated by filtration, to be evaporated, mixed with coal and dried before distillation. This plan is followed in the match factories.

There are three *modifications* of phosphorus.

(*1*). *Common, pale-colored, phosphorus* which crystallizes in octahedrons has essentially the properties already given. Specific gravity = 1.83 at 10° C. Above 45° C., that is, in the liquid state, the specific gravity decreases considerably; with the temperature at 100° C. it is 1.695; at 200° C. = 1.603. At the boiling-point = 1.485. Phosphorus boils at 250° C. and distills over in an atmosphere of hydrogen. Rapid cooling of the vapor throws the phosphorus out in a fluffy, snow-white condition (flowers of phosphorus). But it is quite certain that slight volatilization goes on at ordinary temperature. To this volatilization

is probably due the *phosphorescence*, the power to emit light in a dark room. Surrounded by oxygen alone there is no phosphorescence; but the latter phenomenon appears when the oxygen is diluted with nitrogen. Phosphorus ignites at *60° C.* in air. Rubbing on a rough surface causes ignition (matches). Mixed with $KClO^3$ a very explosive substance results (lucifer matches).

Phosphorus is poison to man and animals when brought into the stomach or esophagus. Every particle of the phosphorus causes an intense local inflammation of the membrane, hence great pain and shock, which result in death. 0.2 gram may be a fatal dose for an adult person. Emptying the stomach by emetics and the pump may save the life in some cases. The workmen in match factories are known to suffer from necrosis of the teeth, the gums and the jaw-bones themselves. Burns made by burning phosphorus on the fingers have even been fatal. Wash out such wounds with utmost haste with a dilute water solution of bleaching lime, or bleaching soda (crude Javelle).

The best solvent for the active form of phosphorus is carbon disulfid.

(2). *Amorphous red phosphorus.* Sunlight, especially the violet portion of it, or heat plus pressure, or the electric current, changes the ordinary phosphorus more or less rapidly into the amorphous modification. In the factories the change is brought about by keeping the yellow phosphorus for 10 days at a steady temperature of 260° C.

The amorphous red phosphorus is not poisonous. It does not melt even at red heat but volatilizes. It is *not* soluble in CS^2 nor in KOH. It appears as a scarlet or as a purplish-red, pulverulent mass, sometimes brown-red. In bulk it shows sometimes a weak metallic luster, more often no luster at all. It has neither taste nor odor, does not show phosphorescence. It ignites at 260° C. It forms with $KClO^3$, with PbO^2, and with MnO^2, mixtures which ignite by blows or friction. It is the only phosphorus now used in matches, or on the friction surfaces of safety match boxes.

(*3*). *Black crystallized phosphorus.* By heating red phosphorus in a vacuum to 447° C. it is obtained as a violet-black mass of conchoidal fracture, or by fusing together in a vacuum phosphorus and metallic lead. After cooling one finds long-stretched rhombohedrons, black in reflected light, red in transmitted light. This phosphorus has a specific gravity of 2.34.

Atomic weight of phosphorus, P = 31. The determinations of the vapor density lead to 62. We assume therefore that the element in the free state is P^2. According to the combinations into which phosphorus enters with the non-metals, it is trivalent and pentavalent like nitrogen.

The oxyds of phosphorus are P^2O^5, P^2O^3.

Phosphorus pentoxyd, P^2O^5, a colorless, vitreous solid or colorless triclinic crystals. Dissolves in water. Is very hygroscopic (goes slowly into a syrup when standing in moist air), hence it is often

used to dry gases. It has no odor, but a very *sour* taste. Is sometimes called *anhydrous phosphoric acid*. Volatilizes partly at 250° C. But when heated quickly it changes its nature by polymerization (aggregation of molecules) and is much less volatile.

Preparation. By igniting phosphorus in a flask in a current of perfectly dry air. The product is a mass of minute snowy-white crystals. For larger quantities a tinned sheet-iron cylinder is substituted for the flask.

Phosphoric acids. It was Graham who first demonstrated that the pentoxyd can form 3 hydrates and that these hydrates possess very distinct properties. We distinguish these hydrates thus: The trihydrate, $3H^2O.P^2O^5$, the dihydrate, $2H^2O.P^2O^5$ and the monohydrate, $H^2O.P^2O^5$. We translate these hydrates into the radical expressions or hydrogen acids thus:

Trihydrate, $3H^2O.P^2O^5 = 2H^3(PO^4) =$
orthophosphoric acid.
Dihydrate, $2H^2O.P^2O^5 = H^4(P^2O^7) =$
pyrophosphoric acid.
Monohydrate, $H^2O.P^2O^5 = 2H(PO^3) =$
metaphosphoric acid.

Orthophosphoric acid, $H^3(PO^4)$. Orthorhombic, colorless crystals, or a thick syrup of specific gravity $= 1.88$. Strong acid reaction; easily soluble in water. Gives green coloration to a flame.

Preparation. (1). By acting with HNO^3 (specific

gravity $= 1.2$) upon ordinary phosphorus in a glass retort, (1 phosphorus, 10 acid), at such a temperature that lively action ensues, but not a violent one, (because explosions may set in). After all the phosphorus has disappeared heat to boiling and distill over about 7 parts of the HNO^3. The distillate has a specific gravity of 1.1–1.14 and may be used for another operation by adding enough concentrated acid to bring gravity up to 1.2. Pour the liquid from the retort into an evaporating dish and evaporate carefully to syrup, or until all HNO^3 has been removed. Sometimes there occurs during this stage another disengagement of NO from the fact that some P^2O^3 is still present. The temperature may be brought to $188°$ C. but not higher, for pyro-phosphoric acid may form. By adding some alcohol the remainder of HNO^3 may be removed more easily. The syrup of $H^3(PO^4)$ is called *glacial phosphoric acid.*

(2). By acting upon red amorphous phosphorus with concentrated HNO^3. The oxydation is more rapid and can be carried on in a beaker glass.

Orthophosphates. The orthophosphoric acid can form 3 series of salts as follows:

Monads, $Na^3(PO^4)$, $HNa^2(PO^4)$, $H^2Na(PO^4)$.

Diads, $Ca^3(PO^4)^2$, $Ca^2H^2(PO^4)^2$, $CaH^4(PO^4)^2$.

Triads, $Al^3(PO^4)^3$, $Al^2H^3(PO^4)^3$, $AlH^6(PO^4)^3$.

The radical (PO^4) is trivalent, hence $Na^3(PO^4)$ is a fully saturated combination and so is $Al(PO^4)$, because aluminum is trivalent. But in order to bring

out the partially saturated series (Al^2H^3) and (AlH^6), we must treble the saturated molecule into $Al^3(PO^4)^3$. Any diad 'metal will form orthophosphates similar to calcium. For example, copper will make $Cu^3(PO^4)^2$, $Cu^2H^2(PO^4)^2$, $CuH^4(PO^4)^2$. The three series are sometimes called *basic, neutral, acid.*

$Cu^3(PO^4)^2$ is basic copper orthophosphate.

$Cu^2H^2(PO^4)$ is neutral copper orthophosphate.

$CuH^4(PO^4)$ is acid copper orthophosphate.

The orthophosphates of potassium, sodium, ammonium are all soluble in water and all can be crystallized. The most common of them, because most easily obtainable, is $Na^2H(PO^4) + 12H^2O$ in monoclinic crystals, and $H.NH^4.Na(PO^4) + 4H^2O$, also monoclinic crystals. The latter salt goes under the names: *salt of phosphorus,* and *microcosmic salt.* This salt fuses into a perfect glass and dissolves at red heat most of the metallic oxyds, giving with some of them transparent glasses of constant color. Hence we utilize this salt as a flux in blow-pipe analysis.

Preparation of microcosmic salt. Dissolve 353 grams of the crystals of $Na^2HPO^4 + 12H^2O$ and 53.5 grams of NH^4Cl (sal ammoniac) in 1700 c.c. of warm water, filter and evaporate until a film of crystals forms at the surface. Let stand for several days in a cool place. A large crop of the microcosmic salt will have been formed. Drain crystals from mother liquor. Dissolve again in water and crystallize, repeating the recrystallization twice. Then you will have crystals sufficiently free from NaCl to answer for blow-pipe work. Reaction:

$$Na^2HPO^4 + water + NH^4Cl = NH^4.NaHPO^4 + water + NaCl.$$
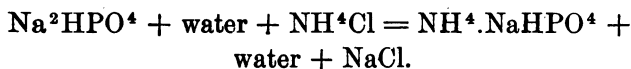
NaCl remaining in the crystals causes the bead, after fusion, to become white and opaque.

Insoluble orthophosphates. The neutral solutions of all the metals are precipitated by adding a solution of any alkali phosphate (K, Na, NH^4). These precipitates are soluble in dilute acids—even acetic acid. Two of these precipitates are of special interest because by means of them we distinguish orthophosphoric acid from other acids.

(1). *Silver orthophosphate, $Ag^3(PO^4)$,* a *yellow* flocculent precipitate. The solution must be *neutral* before $AgNO^3$ is added to the unknown.

(2). *Ammonium-magnesium orthophosphate, $NH^4.Mg$-(PO^4),* a colorless, granular or crystalline precipitate which forms when $MgCl^2$ or $MgSO^4$ solution is added to a slightly ammoniacal solution of an orthophosphate.

The most delicate or sensitive reagent for orthophosphate is the so-called *molybdic solution.* This is a solution of $(NH^4)^2MoO^4$—ammonium molybdate —in HNO^3, specific gravity 1.2; the solution is pale yellow or colorless. Any metallic phosphate is first dissolved in a little HNO^3, or any unknown substance is heated with HNO^3, water added and after filtering 1 volume of the molybdic solution is added. The temperature of the liquid is brought to about 50° C., and the liquid shaken rapidly. A fine granular, citron-yellow precipitate falls if a phosphate be present. The precipitate is $(NH^4)^2$-

$H(PO^4).10MoO^3 + 1\frac{1}{2}H^2O =$ *ammonium-hydrogen phosphopolymolybdate.*

Pyrophosphoric acid, $H^4(P^2O^7)$, is not known in solid state, only known as an aqueous solution.

Preparation. Heat the salt $Na^2H(PO^4) + 12aq.$ in a crucible until all the water is driven out and then to redness for a short time. Reaction :

$$2Na^2H(PO^4) + \text{heat} = Na^4P^2O^7 + H^2O.$$
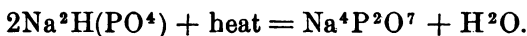
Dissolve in water without heating. To solution add $Pb\bar{A}^2$ (lead acetate); a white precipitate $Pb^2(P^2O^7)$ falls. Filter and wash. Suspend the precipitate in water and pass H^2S into the liquid; then you obtain $Pb^2(P^2O^7) + 2H^2S = 2PbS + H^4(P^4O^7)$, which are separated by filtering.

Properties. (1). When the acid is neutralized with NH^4OH and $AgNO^3$ is added, a *white* flocculent precipitate falls (not yellow as with an orthophosphate). (2). $MgCl^2$ does not produce a precipitate.

When the precipitate $MgNH^4(PO^4)$ (see above) is ignited $Mg^2(P^2O^7)$ magnesium pyrophosphate is left behind. A solution of pyrophosphoric acid reverts into orthophosphoric acid by boiling for several hours.

Metaphosphoric acid, $H(PO^3)$. A colorless glassy substance.

Preparation. (1) By dissolving P^2O^5 in cold water. (2) By heating the syrup of H^3PO^4, thus $H^3PO^4 + \text{heat} = H^2O + H(PO^3)$. (3) By fusing the microcosmic salt at a red heat we get

$Na(NH^4)H(PO^4) + heat = Na(PO^3) + NH^3 + H^2O$
sodium   metaphosphate + ammonia + water.   The
characteristics of metaphosphoric acid are as fol-
lows : (a) the acid solution causes coagulation (curd-
ling) in a water solution of albumen.   (Neither
ortho- nor pyrophosphoric acid coagulates the albu-
men.)   (b) When the solution is neutralized with
NH^4HO, $AgNO^3$ solution gives a white gela-
tinous precipitate.   (c) When a solution of $Na(PO^3)$
is added to neutral salts of the metals, a precipitate
forms at first, but dissolves on further addition of
the metaphosphate.   Some of the precipitates sepa-
rate like tough resin, some separate as oily liquids.

Phosphorus trioxyd, P^2O^3.   White snowy aggre-
gates of small crystals often in the shape of trees
or ferns.

Preparation.   Heat phosphorus in a tube until it
ignites, and allow a very slow current of dry air to
pass through the tube.   The oxyd sublimes into a
receiver.   In the dark it remains unchanged.   Sun-
light brings red or orange colors.   In warm oxygen
it ignites and changes to P^2O^5.

It smells like phosphorus.   Some authors say it
is poisonous, others say it is not ; I, myself, think it
is poisonous.   Very slightly soluble in water.

Phosphorous acid, hydrogen phosphite, $H^3(PO^3)$.
Crystalline-white mass or distinct crystals.   Soluble
in water.   Sour taste.   Is a strong deoxydixing
agent.   In salts of gold, silver, copper, mercury, the
acid causes *precipitation of the metal.*

It is a diatomic acid, that is to say, only two of

the hydrogens can be replaced by a metal. There are therefore two series of *phosphites*, $Na^2H(PO^3)$ and $NaH^2.(PO^3)$.

Preparation. (1). By action of dilute HNO^3 upon phosphorus. (2). By the action of oxalic acid upon phosphorus trichlorid. Thus:

$$PCl^3 + 3H^2.C^2O^4 = H^3PO^3 + 3HCl + 3CO^2 + 3CO.$$

Hypophosphorous acid, hydrogen hypophosphite, H^3PO^2. A colorless substance in large scales or leaves. Its solution in water is even more deoxydizing than the preceding phosphorous acid. It is a monobasic acid. Only one of the three hydrogens can be replaced by a metal. Thus $NaH^2(PO^2)$ or still better $Na(HPO^2H)$ = sodium hypophosphite, or $Ba(HPO^2H)^2$ = barium hypophosphite. The hypophosphites have been recommended as very active stimulants of the nerves and the brain (humbug).

Preparation. $3KHO + 4P + 3H^2O = 3KH^2PO^2 + PH^3$. This means that phosphorus in presence of water and KHO will form potassium hypophosphite plus phosphine (PH^3). $Ca(HO)^2$ and $Ba(HO)^2$ plus P act similarly.

COMBINATIONS OF PHOSPHORUS WITH CHLORINE.

Phosphorus trichlorid, PCl^3. Colorless liquid. Produces white fumes in moist air; refracts the light strongly, smell, penetrating, and the vapor causes tears to flow. Boils at 76° C.

When PCl^3 is poured into cold water it sinks to the bottom and collects like a heavy oil; soon a reaction sets up between the water and the chlorid,

$PCl^3 + 3H^2O = H^3.PO^3 + 3HCl$, the result being a liquid containing phosphorous acid and hydrochloric acid.   Such a solution answers as a deoxydizer.

Preparation. Place in a retort some pieces of dried stick phosphorus (dry with blotting paper), the retort having been previously filled with CO^2 gas. In the tubulus fits a cork, and through this passes a glass tube down to the phosphorus. A receiver is tightly connected with the retort, and is well cooled. Fill now the retort with chlorine, and warm the retort until the phosphorus melts, when the action begins and PCl^3 distills over.

Phosphorus pentachlorid, PCl⁵.   A colorless solid. Peculiar odor, fumes at the air. With little water it decomposes into HCl and $POCl^3$. It is often used in synthetic laboratory work to put Cl into complex molecules. With sodium it gives $2NaCl + PCl^3$, and the same with other metals. With much water it decomposes into phosphoric acid and HCl.

$$PCl^5 + 4H^2O = 5HCl + H^3(PO^4), \text{ orthophosphoric}$$
$$\text{acid.}$$

Preparation. By acting with excess of Cl upon PCl^3. There are, of less importance, PBr^3, PBr^5, PI^3, PI^5, PF^5.

Phosphine, hydrogen phosphid, PH³. A gas of disagreeable odor, somewhat resembling that of garlic. In a dark room the gas gives out a pale light like phosphorus itself. It causes a taste on the tongue. Sunlight decomposes the gas into hydrogen and red amorphous phosphorus. The gas

is poisonous because the blood absorbs it like
H(CN). Air containing 0.25 per cent. PH^3 kills
animals in 5–10 minutes. Phosphine ignites in air
at 149° C.; the flame is white and yields white
smoke. But sometimes the gas is *self-igniting*. This
self-ignition is attributed to the admixture of an-
other compound PH^2, which latter forms only under
specific conditions. When phosphine gas is passed
into solutions of Ag, Hg, Cu, Pb, Bi, Au salts, the
metals are thrown out; or phosphids of the metals
are formed. PH^3 in a solution of $AgNO^3$ + water
causes first a yellow precipitate of $Ag^3P.3AgNO^3$ (?
doubtful composition), but black Ag^3P results ulti-
mately.

Preparation. (1). Place 5–10 grams of stick phos-
phorus into a 150 c.c. flask. Fill the flask with
KOH solution (1:5) up to the stopper. The latter
carries one evolution tube, bent so that it can be
made to dip under water in a dish or beaker glass.
(The flask is to be filled completely to avoid ex-
plosion with air). On heating the flask the gas
evolution will set in, and if the water in the dish be
warm, each gas bubble will ignite as it breaks over
the water, and will form a ring of smoke in the air.
(2). Place the phosphorus in the flask as before, but
fill the flask with an *alcoholic* solution of KOH. (70
per cent. alcohol.) The gas will *not ignite* by itself.
The reason for this is that the self-igniting PH^2 re-
mains dissolved in the alcohol; does not mix with
the gas PH^3. In both these actions the PH^3 is
generated by the reaction

$$3KHO + 4P + 3H_2O = PH_3 + 3KH_2PO_2.$$
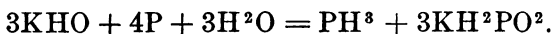
(3). Prepare Na_3P by fusing together sodium and phosphorus. Or by fusing together

$$3Na_2CO_3 + Ca_3(PO_4)_2 + 8Mg = 2Na_3P + 3CaCO_3 + 8MgO.$$
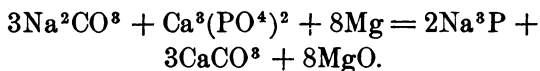
In either case you get Na_3P and if a drop of water touches Na_3P then phosphine will be disengaged (noticed by strong odor), and $NaHO$ will form:

$$Na_3P + 3H_2O = PH_3 + 3NaHO.$$
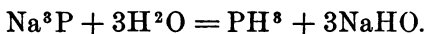
Metallic magnesium can be carried much better than sodium because it does not oxydize so easily at ordinary temperature. Hence the last reaction is the one best adapted to test an unknown mineral for phosphorus, in the field, in the operation of blow-pipe analysis. We call it the *phosphine reaction.* It is all done in a small ignition tube.

Composition of PH_3. Phosphine breaks up readily at a red heat into $P + H$. If 20 c.c. of phosphine are collected over mercury in a eudiometer (see ammonia) and the spark is sent through it, complete dissociation results in from 6 to 10 minutes, when the volume has increased to 30 c.c. Phosphorus covers the surface of the tube and the gas consists entirely of hydrogen. Now since the volume of solid phosphorus is so small as to be negligible it follows that 20 c.c. of phosphine contain 30 c.c. of hydrogen and 10 c.c. of phosphorus gas. Hence PH_3.

Phosphonium, PH_4, corresponds to *ammonium,* NH_4, and is only known hypothetically. Because

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PH^3 combines by simple addition with HCl, giving PH^4Cl (colorless crystals below 20° C.).

Liquid hydrogen phosphid, PH^2. A colorless liquid, not soluble in water. In contact with air ignites instantaneously. Forms when Ca^3P^2 is decomposed with H^2O and the resulting gas is carried through a U-tube standing in the freezing mixture. At the same time with the liquid PH^2, condenses a solid substance which has probably the composition P^2H. Phosphorus combines directly with all metals, yielding *metallic phosphids*. Of practical importance are the phosphids of iron (in the metallurgy of iron and steel) and tin phosphid, Sn^4P, beautiful silver-white crystals (in the manufacture of *phosphorbronze*).

APPENDIX.

THE CHEMICAL ELEMENTS, THEIR SYMBOLS, EQUIVALENTS AND SPECIFIC GRAVITIES.

Name.	Symbol.	Mass Unit Weight.	Specific Gravity.
Aluminium	Al.	27.5	2.56
Antimony.	Sb.	122.0	6.70
Arsenic.	As.	75.0	5.70
Barium.	Ba.	137.0	4.00
Bismuth	Bi.	210.0	9.7
Boron	B.	11.0	2.63
Bromine	Br.	80.0	5.54
Cadmium	Cd.	112.0	8.60
Caesium	Cs.	133.0	1.88
Calcium	Ca.	40.0	1.58
Carbon	C.	12.0	3.50
Cerium	Ce.	92.0	6.68
Chlorine	Cl.	35.5	2.45
Chromium	Cr.	52.5	6.81
Cobalt	Co.	58.8	7.7
Columbium	Cb.	184.8	6.00
Copper	Cu.	63.0	8.96
Didymium	Di.	96.0	6.54
Erbium	E.	112.6	—
Fluorine	F.	19.0	1.32
Gallium	Ga.	69.9	5.9
Glucinum.	Gl.	9.5	2.1
Gold (Aurum).	Au.	196.0	19.3
Hydrogen	H.	1.0	0.069
Indium	In.	113.4	7.4
Iodine	I.	127.0	4.94
Iridium	Ir.	198.0	21.15
Iron (Ferrum).	Fe.	56.0	7.79
Lanthanum	La.	90.2	11.37
Lead (Plumbum)	Pb.	207.0	11.44
Lithium	Li.	7.0	0.59

Name.	Symbol.	Atomic Weight.	Specific Gravity.
Magnesium	Mg.	24.0	1.75
Manganese	Mn.	55.0	8.01
Mercury (Hydrargyrum) . .	Hg.	200.0	13.59
Molybdenum	Mb.	96.0	8.60
Nickel	Ni.	58.8	8.60
Niobium	Nb.	94.0	6.27
Nitrogen	N.	14.0	0.972
Osmium	Os.	199.0	21.40
Oxygen	O.	16.0	1.105
Palladium	Pd.	106.5	11.60
Phosphorus	P.	31.0	1 83
Platinum	Pt.	197.4	21.53
Potassium (Kalium) . . .	K.	39.0	0.865
Rhodium	Ro.	104.3	12.1
Rubidium	Rb.	85.4	1.52
Ruthenium	Ru.	104.4	11.4
Selenium	Se.	79.5	4.78
Silicon	Si.	28.0	2.49
Silver (Argentum)	Ag.	108.0	10.5
Sodium (Natrium)	Na.	23.0	0.972
Strontium	Sr.	87.6	2 54
Sulphur	S.	32.0	2.05
Tantalum	Ta.	182.0	10 78
Tellurium	Te.	129.0	6.02
Thallium	Tl.	204.0	11.91
Thorium	Th.	115.7	7.8
Tin (Stannum)	Sn.	118.0	7.28
Titanium	Ti.	50.0	4.3
Tungsten (Wolfram) . . .	W.	184.0	17.6
Uranium	U.	120.0	18.4
Vanadium	V.	51.3	5 50
Yttrium	Y.	61.7	—
Zinc	Zn.	65.0	7.14
Zirconium	Zr.	89.5	4.15

TABLE FOR THE COMPARISON OF THE SCALES OF RÉAUMUR'S, CELSIUS'S, AND FAHRENHEIT'S THERMOMETERS.

Réaumur.	Celsius.	Fahrenheit.	Réaumur.	Celsius.	Fahrenheit.
—15	—18.75	—	33	+41.25	+106.25
14	17.50	+0.50	34	42.50	108.50
13	16.25	2.75	35	43.75	110.75
12	15.00	5.00	36	45.00	113.00
11	13.75	7.25	37	46.25	115.25
10	12.50	9.50	38	47.50	117.50
9	11 25	11.75	39	48.75	119.75
8	10.00	14.00	40	50.00	122.00
7	8.75	16.25	41	51.25	124.25
6	7.50	18.50	42	52.50	126.50
5	· 6.25	20.75	43	53.75	128.75
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Rules for the Conversion of the Different Thermometer
Degrees into each other.

The thermometers referred to in the table are gradu-
ated so that the range of temperature, between the
freezing and boiling points of water, is divided by
Fahrenheit's scale into 180 (from 32° to 212°) by
Celsius's into 100 (from 0 to 100°), and by that of
Réaumur into 80 (from 0 to 80°) portions or degrees.

The spaces occupied by a degree of each scale are
consequently as $\frac{1}{9}$, $\frac{1}{5}$ and $\frac{1}{4}$ respectively, or as 1, 1.8
and 2.25; and the number of degrees denoting the same
temperature, by the three scales, when reduced to a
common point of departure by subtracting 32 from
Fahrenheit's, are as 9, 5, and 4. Hence we derive the
following equivalents :

A degree of Fahrenheit is equal to 0.5 of Celsius's,
or to 0.4 of Réaumur's; a degree of Celsius's is equal to
1.8 of Fahrenheit's, or to 0.8 of Réaumur's; and a de-
gree of Réaumur's is equal to 2.25 of Fahrenheit's, or
to 1.25 of Celsius's.

To convert degrees of Fahrenheit into Celsius's or
Réaumur's, subtract 32 and multiply the remainder by
$\frac{5}{9}$ for Celsius's, or, $\frac{4}{9}$ for Réaumur's.

To convert degrees of Celsius's or Réaumur's into
Fahrenheit's, multiply Celsius's by $\frac{9}{5}$, or Réaumur's
by $\frac{9}{4}$, as the case may be, and add 32 to the product.

TABLE OF THE LITER WEIGHTS OF THE GASES.

Temp. 0° C. and 760 Mm. Pressure.

1 liter of air weighs.	. . . .	1.29300	Gms.
"	CO. "	. . . .	1.25078	"
"	CO². "	. . . .	1.96500	"
"	O. "	. . . .	1.42910	"
"	H. "	. . . .	0.08988	"
"	N. "	. . . .	1.25070	"
"	NO. "	. . . .	1.34260	"
"	NO². "	. . . .	2.05440	"
"	N²O. "	. . . .	1.96770	"
"	NH³. "	. . . .	0.76170	"
"	Cl. "	. . . .	3.17240	"
"	HCl. "	. . . .	1.62850	"
"	H²S. "	. . . .	1.52100	"
"	SO². "	. . . .	2.86150	"
"	CH⁴. "	. . . .	0.71570	"
"	steam* "	. . . .	0.58960	"
"	C²H². "	. . . .	1.16200	"
"	Br. "	. . . .	7.14259	"
"	I. "	. . . .	11.27100	"
"	S. "	. . . .	2.84300	"
"	P. "	. . . .	5.63180	"
"	Hg. "	. . . .	9.02100	"
"	HI. "	. . . .	5.71067	"
"	HBr. "	. . . .	3.61607	"
"	C²N². "	. . . .	2.32653	"

* At 100° C. and 760 Mm.

The values in the above table may be calculated from the relation between the molecular weight in grams of the substance and its liter weight. This relation may be expressed as an equation thus :

$$\frac{\text{weight of gram-molecule}}{\text{weight of a liter}} = \text{constant} = 22.38,$$

or liter weight $= \dfrac{\text{weight of gram molecule.}}{22.38}$

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